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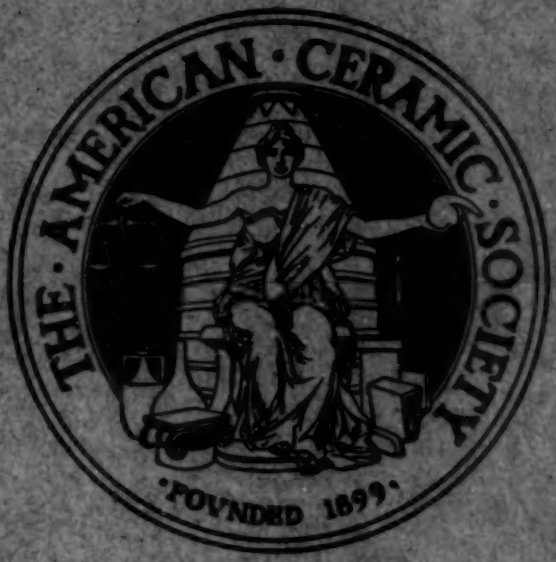


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ABSTRACTS
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Thirty-Fifth
Annual Meeting

# American
# Ceramic Society

Hotel Netherland Plaza

Cincinnati, Ohio

Week of February Eleven
1934

Eight Simultaneous Division Meetings

All on One Floor

# DIFFICULTIES IN FIRING DECORATED WHITEWARE*

By J. T. Robson

ABSTRACT

Some of the problems encountered in firing decorated whiteware are discussed. Both commercial and laboratory tests were conducted to show the cause of difficulties and their prevention. The subjects discussed are (1) "spit-out" or blistered glaze, (2) prevention of crazed or dunted glaze, (3) firing of selenium red overglaze, and (4) prevention of specks in decorating or overglazing one-fired whiteware.

## I. Glaze Spit-Out

"Spit-out" or blistering of the glaze in the decorating kiln occurs when old glost ware is used or when the decorating temperature is too high. While this is true, from experience and the following tests it is believed that a frequent cause of spit-out is the kiln atmosphere itself. Probably the superheated steam from the products of combustion which contain two cubic feet of water vapor for every cubic foot of gas burned is the primary cause.

Ware stored a long time absorbs moisture slowly through glaze imperfections and the glost sagger pin spots. In the rapid firing cycle of the decorating kiln, this moisture does not have sufficient time to pass out through the glaze openings through which it entered. Some of the moisture may actually enter into chemical combination, rehydrating some of the clay, which retards its expulsion from the ware. As a result, the moisture, in part at least, forms steam which actually bursts out through the glaze causing blisters or spit-out.

Under a magnifying glass a fractured piece of glazed semiporcelain shows bubbles in the glaze. This is especially marked with a spit-out glaze. The degree of spit-out depends not only on the number and size of the bubbles but also on the extent to which these bubbles have approached the surface of the glaze. In the case of incipient spit-out the bubbles have barely reached the surface of the glaze. In exaggerated spit-out many of the bubbles have reached the glaze surface and broken through, leaving actual craters on the glaze surface. Figure 1 shows a view of a very bad case of spit-out. Figure 2 is a cross-section of this same piece. Note how the bubbles exist throughout the glaze.

A lower temperature decorating fire sometimes prevents spit-out because the bubbles formed have not come close enough to the surface of the glaze to become visible. This might be caused by too low a temperature to create enough pressure within the bubbles or to soften or lower sufficiently the viscosity of the glaze for the bubbles to escape.

At first it was thought that spit-out was due either to underfired glaze from the glost kiln or too rapid firing in the decorating kiln. The following tests show that this is not the case, but that kiln atmosphere has a decided effect on spit-out.

**(1) Test No. 1** One piece of a dull green or underfired glazed 5-inch plate and one piece of a slightly spit-out dull ivory glazed 7-inch plate from the direct-fired decorating kiln were fired in a gas-fired muffle kiln to 1410°F in one hour and cooled in $1^{3}/_{4}$ hours, a total firing

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* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (White Wares Division).

cycle of $2^3/_4$ hours. The green piece did not spit-out nor did the spit-out blisters increase in number or size on the ivory piece.

**(2) Test No. 2** Two pieces of well-fired ivory glazed 7-inch plates were fired in the gas-fired muffle kiln to 1410°F in 45 minutes. One piece was removed immediately and the other piece cooled for 2 hours. After firing there was no sign of spit-out in the glaze.

**(3) Test No. 3** Pieces of the same ware as used in Test No. 1 were fired in the gas-fired muffle kiln to 1810°F in 45 minutes and cooled in 2 hours and 35 minutes. After firing, the spit-out in the ivory-glazed piece partially disappeared and no change took place in the green-glazed piece.

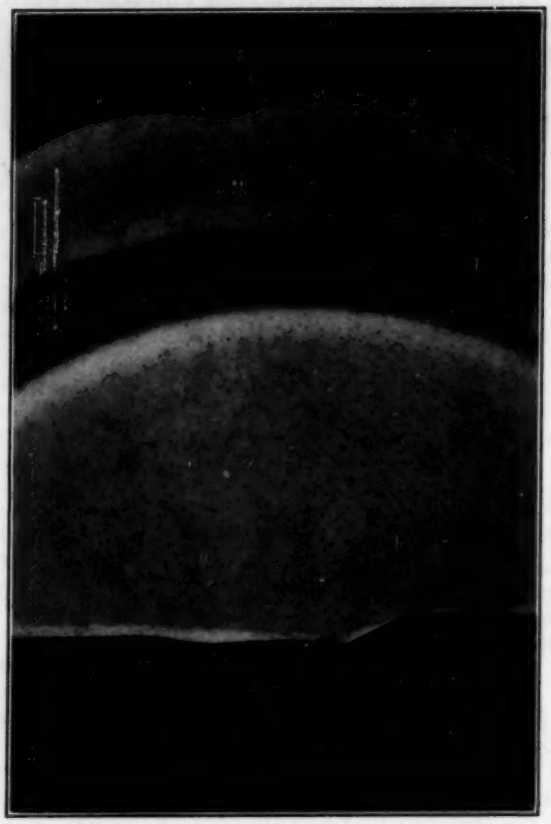

FIG. 1.

**(4) Test No. 4** One-half of a 5-inch plate with the dull green glaze and a piece of 7-inch plate with the dull ivory spit-out glaze were fired in a gas-fired muffle kiln to 2120°F, cone 7 down in 10 hours, and cooled in $14^1/_2$ hours. The results showed the green plate to be a lighter and brighter green. The ivory-glazed piece was also lighter in color and brighter than before the test and all traces of spit-out had disappeared. The glaze naturally showed minute pinholes or an egg-shell effect which did not appear to be excessive on this refired piece and which, prior to refiring, was badly spit-out.

**(5) Conclusions from Tests Nos. 1 to 4** (1) The rate of firing and cooling had no influence in promoting spit-out ware.

(2) Underfiring of the glost ware did not promote spit-out when fired in a muffle kiln.

(3) The dull glazes became brighter when fired harder which is usual.

(4) The spit-out holes partially disappeared at 1810°F and entirely dis-

appeared at cone 7 (2120°F). No doubt they were entirely gone at a temperature between 1810°F and 2120°F.

Since it did not appear to be the maturity of the glaze or the rate of refiring which caused the spit-out, the next point of investigation was that of kiln atmosphere or muffle fire *versus* direct fire.

**(6) Test No. 5** One dull green 7-inch plate and one bright ivory glazed 7-inch plate were fired in a direct gas-fired kiln to 1340°F in 2 hours and 40 minutes and cooled in $3^1/_4$ hours. A long reducing flame was used. After refiring, the ivory-glazed plate was darker in color

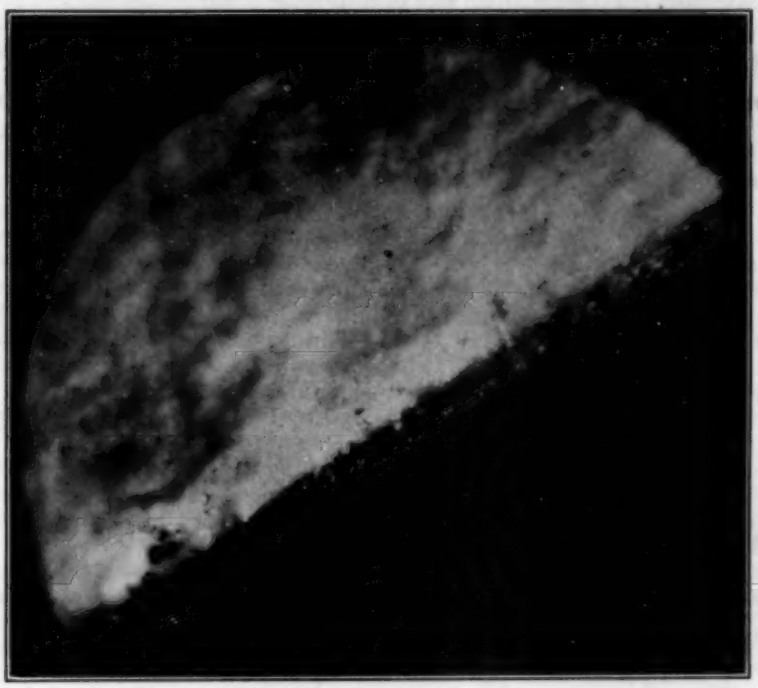

FIG. 2.

due to flashing and was also badly spit-out. The green-glazed plate was darker in color and red on the edges due to reduced copper but no spit-out occurred.

From Test No. 5 it appeared that either the flame touching the ware or the products of combustion in the kiln atmosphere were causing the spit-out. To check this conclusion Test No. 6 was run.

**(7) Test No. 6** This test was run firing 7-inch ivory glazed plates, one slightly dull, one bright, and one that had been previously decorated and fired through a direct-fired decorating kiln. This latter plate had a slight semblance of spit-out prior to refiring in this test. These three plates were fired in a direct gas-fired kiln to 1420°F in $3^3/_4$ hours and cooled in $2^1/_2$ hours. In firing this kiln, care was exercised to make certain that the flame did not strike the ware. At the same time

one fairly dull and one bright 7-inch ivory plate and one dull and one bright 7-inch green plate were fired in a muffle kiln to 1540°F in 3¼ hours and cooled in 3 hours.

In the direct-fire test, all three samples spit-out badly. In the muffle fire, no change in the glaze could be noted.

**(8) Test No. 7** This test was run in a direct gas-fired kiln, using a long flame and reducing conditions. One dull green 7-inch plate was fired to 1410°F in 2½ hours and cooled 12½ hours before removing from the kiln. After the test, the plate was a fairly bright reduced copper red color with no sign of spit-out.

**(9) Conclusions from Tests Nos. 5 to 7** The results of Tests Nos. 5, 6, and 7 tend to show that (1) the copper green glaze does not spit-out with different atmospheric conditions, and (2) the kiln atmosphere is the vital factor causing spit-out ware.

It was not the presence of flame or flashing against the ware but primarily the atmospheric condition itself or products of combustion that caused spit-out.

**(10) Test No. 8** Two pieces broken from two well-glazed ivory 7-inch plates were boiled several hours in water until the darkening underneath the glaze showed one piece to be entirely saturated with water and the other piece to be saturated to within ½ inch of the outside edge. These two pieces together with a dry piece placed on top were fired in the muffle to 1410°F in 25 minutes and removed immediately from the kiln. After firing, the two pieces which had been soaked in water were spit-out considerably. The dry piece did not spit-out.

These results check with those obtained by Lintz,[1] who found that spit-out was accelerated by soaking the ware in water for three hours. He took a number of 7-inch glost plates, soaked them in water for three hours, and fired them through the decorating kiln all on the same car deck to insure exact firing conditions. In all cases those plates having the highest absorption spit-out badly while those of normal absorption showed no spit-out or only a slight tendency. This shows that the greater the volume of water absorbed by the glazed ware, the greater the tendency to spit-out.

**(11) Test No. 9** To check the effect on spit-out of steam in the products of combustion, two pieces of well-fired glazed ivory 7-inch plates were placed in the muffle and steam was conducted into the muffle through a ½-inch heated copper tube. The kiln was fired to 1410°F in 45 minutes and steam admitted the last 20 minutes from 1050 to 1410°F.

After firing, the pieces were removed immediately from the kiln. The piece of ware directly under the copper tube steam outlet was badly spit-out and the other piece slightly spit-out.

**(12) Test No. 10** Two green glazed 7-inch plates, one dark and one light, and two ivory glazed plates were run through a commercial muffle decorating kiln in 14½ hours at a maximum temperature of 1320°F. There was no sign of spit-out on this ware. The same ivory-glazed ware, when fired through a direct-fired decorating kiln, spit-out badly at a temperature even as low as 1180°F.

**(13) Test No. 11** A plant using a continuous muffle decorating kiln was having excessive spit-out ware. This kiln had been

[1] Ceramic Engineer, Taylor, Smith & Taylor Co.

operated intermittently for about two years. When shut down, the kiln was allowed to cool rapidly to room temperature and when started back to heat, the temperature was raised as rapidly as possible, all of which facilitated opening up between the muffle plates. The kiln was shut down and the cracks were sealed. When again started the spit-out ware had practically disappeared.

**(14) Test No. 12** A continuous muffle decorating kiln similar to that in Test No. 11 had been operating for three years with practically no spit-out ware of any kind on any of the patterns. The heating and cooling of the muffles in this kiln had always been done gradually in order to insure a tight muffle at all times, which probably accounts for the success of this kiln in preventing spit-out ware. The amount of spit-out ware in the periodic muffles was far in excess of that in the tunnel kiln. Of course the variation in firing cycle and temperature variation throughout the muffle of the periodic decorator could have a decided influence on this, but this plant had the normal amount of spit-out ware in the periodic decorator, whereas in the tunnel decorator it was less than that of any plant tested.

Some ware was taken from the plant reported in Test No. 11 at the time spit-out was occurring. This was fired through the Test No. 12 kiln with no sign of spit-out although the temperature and firing cycle were the same.

**(15) General Conclusion from Tests Nos. 1 to 12** All of the above tests tend to show that the kiln atmosphere is of prime importance in causing spit-out ware.

## II. Crazed Ware

Twelve- and fourteen-inch dishes that had been glost-fired six to twenty-four months prior to decorating gave an excessive loss in the decorating kiln due to crazing of the glaze. The glaze on some pieces had cracked or crazed during the heating process. This could be determined after firing because the glaze crack was not sharp but rounded or partially healed over at the edges of the crack due to later softening at the higher temperature.

A majority of the ware, however, showed an almost invisible fine glaze dunt or craze. After several unsuccessful attempts at changing the kiln, drafts, firing cycle, and temperature curve, a dozen 14-inch dishes that had been glost-fired nearly two years previously were refired through the glost kiln at cone 4. These were then decorated and fired through the decorating kiln entirely satisfactorily.

This procedure is followed with all old glost dishes or platters above 10 inches. It has entirely eliminated any sign of glaze crack or crazing on the ware.

## III. Selenium Glaze

A red selenium overglaze, when fired through the decorating kiln, usually came out an uneven color ranging from almost black to red-brown to bright red. It seemed that raising or lowering the temperature or changing the firing cycle did not correct this trouble.

Previous experience in firing another type of selenium-glazed ware had shown that when placed too close together there was a tendency for the

glaze to darken in streaks due to volatilization and condensation from one to the other.

Bearing this in mind, seven pieces of red selenium overglazed ware were placed on the lower deck with no bat or shelf above and each piece was spaced about 3 inches apart. This not only kept the ware separated enough to avoid the condensation of the selenium or lead fumes, but also kept the ware down below the sizing fumes from the decal ware ahead of it in the tunnel.

The result of this test showed all seven pieces to be glazed perfectly bright red.

To check the effect of temperature and firing cycle on this selenium overglaze, the following tests were run on lamp bases about 4 inches square.

(1) **Test No. 1** The sample was fired to 1330°F in 30 minutes when the temperature was immediately dropped and the piece cooled in 45 minutes, making a total firing cycle of 75 minutes. The overglaze was a bright red entirely satisfactory.

(2) **Test No. 2** The maximum temperature in the commercial kiln was applied to the ware for a period of about $1^1/_2$ hours on normal schedule. This test was run holding the temperature rise from 1340 to 1420°F for $2^1/_4$ hours and a cooling time of one hour. The overglaze was an even bright red, as in Test No. 1.

(3) **Test No. 3** The sample was fired to a maximum temperature of 1680°F in 30 minutes and cooled in one hour. At this temperature the glaze was an uneven red to black due to overfiring.

(4) **Test No. 4** The sample was fired to a maximum temperature of 1500°F when the heat was immediately shut off and the kiln cooled slowly for two hours. The result was a satisfactory red as in Test No. 1.

(5) **Test No. 5** To check the possible effect of the varnish fumes from the decal in causing this discoloration, two tests similar in every respect, except the maximum temperature, were run.

A sample to which the red selenium overglaze had been applied on four sides was painted with varnish every place except over the selenium glaze. Then two crucibles of varnish were placed on either side of the piece. This was fired to 1420°F after which the piece showed a good red overglaze on all four sides.

A similar test fired to 1480°F showed a satisfactory red overglaze on all four sides.

(6) **Test No. 6** Two pieces painted with overglaze on all four sides were set in the kiln with one side of one piece within $^1/_8$ inch of the other. These were fired to 1420°F; after firing, the two sides which had been adjacent to one another were badly discolored.

(7) **Conclusions** (1) The temperature can be varied considerably and yet a satisfactory selenium red color is obtained.

(2) The time of heat soak is not vital.

(3) The time of cooling has no effect.

(4) Since a $1^1/_4$-hour complete firing cycle in the laboratory kiln gave the same results as a 7-hour cycle in the commercial kiln, it appears that the firing time can be varied considerably.

(5) The presence of decal varnish vapors does not affect the selenium red overglaze.

(6) Due to volatilization and condensation, the "fill," or closeness of placing the ware in the decorating kiln, has a decided effect upon the appearance of a selenium red overglaze.

## IV. Overglaze Specks

Cone 12 one-fired vitrified white-glazed wall tile and bathroom fixtures, when decorated with an ivory overglaze, showed a varying amount of noticeable dark specks in the glaze when removed from the low-temperature decorating kiln.

A close examination of the ware prior to overglazing showed it to be first-class No. 1 grade. No undesirable spots or specks were present and the glaze had not only good color but good texture as well.

Various reasons had been advanced for this phenomenon, which had been experienced frequently. Some of these were as follows:

(1) The oil firing atomized fine carbon which deposited on the softened glaze in the heating zone and became so impregnated in the glaze that it could not be burned out.

(2) The atomized carbon was deposited in the glaze in the furnace section itself.

(3) The fine carbon deposited in the glaze in the cooling zone around 1500°F. This was claimed to be the source of trouble by several who reasoned that the cooling and adjacent end of the furnace section were under pressure, making this diffusion of carbon toward the discharging end possible. They evidently lost sight of the fact that, although under pressure, there was a rapid movement of the kiln gases at all times toward the charging end.

(4) A reducing condition existed in the kiln.

(5) Carbon was attacking the ware between saggers due to the fact that this was a direct-fired kiln.

(6) The spraying machine was the cause of these specks.

These were some of the reasons advanced by others for this difficulty prior to this investigation as to the cause.

These specks did not show up on all the ware but on a majority of it.

The only actual prior experience of the writer along this line was in the semiporcelain field. When a heavy oil is used in firing the periodic glost kilns, some of the ware, especially that exposed, comes out dull or "greasy." When this dull glost ware is overglazed or has decal varnish applied and is then fired through the decorating kiln, the ware usually comes out specked black much heavier than were the specks in the above case. This is also true of underfired glost ware. It is due to a carbonaceous deposit from the varnish embedding in the glaze or eventually an actual reduction of the glaze from the carbon in the sizing varnish as was proved by applying sizing varnish to both underfired and greasy glost ware. When fired through the decorating kiln, together with similar unvarnished ware, all ware to which varnish had been applied came out dark, whereas the glaze on the unvarnished ware had not changed. To determine the cause of these specks appearing on the cone 12 glazed ware, the following tests were run.

**(1) Test No. 1** A piece of the specked overglaze tile was first treated with hydrofluoric acid at one end to dissolve the overglaze. Then part of this section was further treated with hydrofluoric

acid to dissolve the white glaze completely. This gave a sample with the overglaze and glaze completely dissolved from one end, the middle portion with just the overglaze dissolved, and the other end untouched.

An examination of this piece showed that the white glaze in the middle portion contained just as many specks as the upper or untouched section. The lower end with glaze and overglaze dissolved showed the body to be clean, containing no specks.

This proved that the specks existed in the glaze itself, but the question of their origination and prevention remained to be solved.

It was hard to conceive that these specks could originate in the original glaze fire and yet be entirely invisible when the white-glazed piece came from the kiln. Upon being refired to 1300 or 1400°F, for some reason they became plainly visible.

**(2) Test No. 2** This test was run on samples both hand-sprayed and machine-sprayed. The samples were fired with oil and gas both muffled and direct-fired. The results are as follows:

| Sample | Glaze application (spray) | Method of firing | Cone (touch) | Remarks |
|---|---|---|---|---|
| (*a*) | Hand | Open in oil-fired kiln | 8 | Underfired, no specks; good clean white |
| (*b*) | Machine | Open in oil-fired kiln | 8 | Underfired, no specks; good clean white |
| (*c*) | Hand | Gas-fired muffle | 12 | Underfired slightly, no specks; good clean white |
| (*d*) | Machine | Gas-fired muffle | 12 | Underfired slightly, no specks; good clean white |
| (*e*) | Hand | Inside sagger; oil-fired kiln | 13 | O.K.; good clean white |
| (*f*) | Machine | Inside sagger; oil-fired kiln | 13 | O.K.; good clean white |
| (*g*) | Hand | Open in oil-fired kiln | 13 | O.K.; good clean white |
| (*h*) | Machine | Open in oil-fired kiln | 13 | O.K.; good clean white |

The above results show that the method of glaze application, hand or machine spraying, did not produce specks apparent after firing.

All trials, whether fired with oil or gas, open or protected, were perfectly clean and white after firing.

The samples fired in the open in the oil-fired kiln were purposely set in the path of the flame from the burner. The kiln was started from room temperature with oil so that during the early stages of firing the glaze-sprayed samples in the open were entirely covered with soot or carbon due to incomplete combustion of the oil. As noted, these samples came out perfectly white with no sign of specks in the glaze.

**(3) Test No. 3** Half of the samples from Test No. 2 were painted across one end with sizing varnish such as is used in overglaze work. They were fired in an electric kiln to 1440°F. After firing, every piece was discolored with numerous specks on the end where the sizing varnish had been applied and the other end showed no specks whatever. The samples (*a*) and (*b*) fired to cone 8 showed more specks than the other samples fired to cones 12 and 13.

**(4) Test No. 4** This was a duplicate of Test No. 3 with the remaining half of the samples. The varnished ends were all discolored with specks as in Test No. 3.

**(5) Conclusion, Tests Nos. 1 to 4** These tests show that the varnish is causing the specks in the glaze even though the glaze was previously fired to cone 13.

The samples fired in the gas-fired muffle and inside the saggers of the oil-fired kiln contained just as many specks as those samples fired in the open in the direct path of the flame of the oil-fired kiln. This, together with the fact that the unvarnished portion of the samples did not speck, shows that the specks are not due to carbon from the fuel being deposited on the pieces during heating or at the maximum heat during the original firing. To show that the cause of specking was not due to carbon deposition on the glaze during cooling, Test No. 5 was run.

**(6) Test No. 5** Four samples were fired rapidly in the laboratory oil-fired kiln. Two pieces were placed inside the sagger and two pieces outside directly in front of the burner. Cone 13 was half down outside and cone 6 down inside the sagger. During cooling, the oil continued burning until the temperature dropped to 1300°F, when it was shut off. All samples were perfectly clean after firing. After applying varnish and firing in the decorating kiln, all samples showed some specks, but the samples fired to cone 13 half down were better than those at cone 6.

**(7) Test No. 6** Sample (*d*) fired in the gas-fired muffle to cone 12 touch and sample (*g*) fired in the open oil-fired kiln to cone 13 touch from Test No. 2 were painted across the other end with varnish. Varnish was also applied to the ends of two pieces of white-glazed wall tile (two-fire), a piece of glazed semiporcelain dinnerware (two-fire), a piece of glazed vitrified china (two-fire), and a piece of wall tile glazed in the laboratory (two-fire). These were dried and fired in the laboratory to 1440°F. After firing, samples (*d*) and (*g*) were the only samples to show specks which were across the end where varnish had been applied. The piece of vitrified china was very much discolored blue-black on the broken or unglazed edge of the body where the varnish, when applied, had run down over the side.

**(8) Test No. 7** To compare one-fired ware with two-fired, as in Test No. 6, this test was run.

A white-glazed porcelain tumbler holder (evidently one-fire, no trade mark) was purchased at a five- and ten-cent store. One-half of this piece was varnished, together with two pieces of one-fired electrical porcelain, a piece of one-fired sanitary ware, and a piece of trim tile supposedly the same glaze and body composition as (*h*), but fired some eight months prior to this specking trouble occurrence. After the varnish had dried, these were fired in the gas-fired muffle to 1440°F. After firing, sample (*h*) was the only one showing the presence of specks. All pieces showed a blue-speck discoloration in the body where the varnish had run down over the unglazed edges when applied. On the tumbler holder and trim tile, there was a large number of specks in this discoloration, whereas in the sanitary ware body, the color was a solid discoloration with no specks present.

**(9) Conclusions, Tests Nos. 5 to 7** (1) Test No. 5 showed that the direct oil firing had no effect in causing these specks at any stage of the firing either in the heating, maturing, or cooling zones.

(2) Test No. 6 showed that at least two-fire glazes in general were not subject to specking. On the broken or unglazed side of the vitrified piece, it showed that in case the varnish was even slightly absorbed in pores, the carbonaceous matter did not burn out at decorating temperatures.

(3) Tests No. 6 and No. 7 showed that there was something inherent in the glaze itself that caused the trouble since the specks did not appear in any other samples either one- or two-fired.

**(10) Test No. 8** In this test, varnish was applied to the unglazed end of two pieces of electrical porcelain, two pieces of porous wall tile, and one piece of semiporcelain dinnerware. The purpose was to see whether vitrified and semiporcelain bodies both showed specks from the varnish. After firing to 1440°F, the semivitreous tile bodies and the semiporcelain piece were perfectly clean with no specks. The two pieces of electrical porcelain or vitrified body were badly discolored and specked.

The reason for vitrified ware showing the discoloration is probably the fact that the pores are so small that air can not enter to oxidize the varnish, whereas in semivitrified ware the larger pores permit ready access of air to the varnish.

If the varnish can thus penetrate into the glaze sufficiently, it will cause specks.

**(11) Test No. 9** To determine if the varnish could penetrate the glaze by adsorption, a drop of a solution of malachite green was placed on the glaze of samples (*b*) and (*e*) (Test No. 2) and the tumbler holder and trim tile (Test No. 7). After two hours, the dye had penetrated sample (*b*) so that it could not be washed off. The dye was not visibly absorbed by the other glazes. This was due to sample (*b*) being underfired at cone 8, but since the specks on the cone 8 samples were more pronounced than the cones 12 and 13 samples, it appeared possible that the varnish actually did penetrate the glaze or get down into the surface sufficiently to be protected from the oxygen of the air.

**(12) Test No. 10** Test No. 10 was run to see whether a reasonably high fire would vitrify the glaze sufficiently to prevent the apparent varnish adsorption.

Two pieces of the unfired glaze-applied tile causing the trouble were fired in a gas-fired muffle to cone 15 started. These were then brushed with sizing varnish and fired to 1440°F after which no specks were visible in the glaze.

**(13) Conclusions, Tests Nos. 8 to 10** (1) Test No. 8 shows that varnish absorbed into fine pores will not burn out at decorating temperature and will result in discoloration due to the carbon residue.

(2) The varnish actually penetrates into the underfired glaze causing specks.

**(14) General Conclusion, Tests Nos. 1 to 10** To prevent these specks after applying varnish, this glaze must be fired up to its maximum limit. The trim tile fired prior to the time this trouble started had been fired on a more rapid schedule which required a higher temperature and apparently made the glaze more resistant to varnish absorption or adsorption.

**(15) Test No. 11** Six sample towel-rack holders and six trim tile were fired through a commercial tile gas-fired bisque kiln

to cone 11 touch, 12 started. All samples fired to a good clean white color. After applying sizing varnish and firing to 1300°F in the gas-fired muffle kiln, all samples showed specks.

Under the microscope the glaze appeared rough and the specks resembled dull black carbon which had deposited in the indentations of the glaze.

**(16) Test No. 12** A piece of tile that was badly specked after being run through the decorating kiln was fired to cone 3. The specks were entirely burned out.

**(17) Test No. 13** Using a different source of tin oxide in the glaze did not alter this tendency to speck when decorated.

**(18) Conclusions, Tests 11 to 13** (1) In Test No. 11 the commercial gas-fired tile again showed that the oil firing was not the cause of specks.

(2) The specks burned out at cone 3 or lower, indicating that they were a carbon deposition.

(3) The tin oxide was not a source of this trouble.

**(19) General Conclusions, Tests Nos. 1 to 13** A study of all these tests showed that the specks were caused by carbon deposition from the varnish in the pores or depressions of the glaze.

The feldspar content of the glaze was therefore increased to make it more glassy or smoother, with no pockets, pores, or depressions to absorb or adsorb the varnish which could not be completely burned out at decorating heat around 1300°F.

Results so far show that this trouble has been entirely eliminated by this procedure as described.

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# THE USE OF AUXILIARY FLUXES IN DINNERWARE BODIES*

By George A. Loomis

ABSTRACT

A plant and laboratory study was made of the use of frits as auxiliary fluxes in dinnerware bodies. The frits were added to a commercial earthenware body. Seven-inch plates of these bodies were jiggered, fired, and glazed at the pottery.

Some practical difficulties encountered were as follows: (1) Due to the progressive solubility of the frits, even when this solubility was slight and only 2 to 4% of the frit was used, the slip was deflocculated and the plasticity of the body was destroyed. This trouble apparently was overcome by using a slight excess of hydrochloric acid in the body slip. (2) The ware of the bodies containing frit warped more than the normal body, especially in the glost fire.

Results of tests of the slips, bodies, and ware are presented.

## I. Introduction

A laboratory study of eutectic glasses as auxiliary fluxes in ceramic bodies by P. F. Collins[1] indicated that small amounts of a very fusible and fluid glass added to an earthenware body would promote an earlier vitrification without causing warpage of the ware such as occurs when the feldspar is increased or when additions are made of raw whiting or magnesite. Collins concluded that an addition of 2 to 4% of this glass would permit (1) firing the ware several cones lower than the normal body for the same absorption, or (2) producing a more vitreous ware by firing to the same cone as for the normal body without increasing the warpage.

The present study considers the practicability and advantages of using eutectic glasses and similar fluxes in certain dinnerware bodies.

## II. Preliminary Studies

### (1) Solubility of the Fluxes

Most of the eutectic glasses which Collins studied were water-soluble to a considerable degree. To reduce this solubility he made the fusions with additions of feldspar. All but one of the glasses used in his final studies had this feldspar addition to the eutectic composition. The present study was started by preparing three of the most promising of these glasses and determining their solubilities. Collins ground the glasses to pass 150-mesh, while those in the present study were ground to pass 200-mesh. The eutectic composition of the glasses with feldspar additions and solubilities was as follows:

| Collins' frit designation | Eutectic composition of glass (%) | Feldspar added (%) | Solubility (g./l. of water) | |
|---|---|---|---|---|
| | | | (present study) | (Collins) |
| 6–F–25 | 20 $CaSiO_3$ 80 $Na_2SiO_3$ | 25 | 15.724 | 8.224 |
| 7–F–0 | 69 $CaSiO_3$ 31 $Na_2SiO_3$ | 0 | 1.784 | 0.836 |
| 13–F–25 | 40 $CaSiO_3$ 60 $Na_2SiO_3$ | 25 | 12.456 | 8.497 |

The solubilities were consistent with those determined by Collins considering the difference in fineness.

Each of these glasses was introduced in a typical earthenware body in an

* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (White Wares Division). Received May 8, 1933.

[1] P. F. Collins, "Auxiliary Fluxes in Ceramic Bodies," *Jour. Amer. Ceram. Soc.*, **15** [1], 17–27 (1932); also Ohio State University, Eng. Expt. Sta. *Bull.*, No. 68.

amount equivalent to 2% of the eutectic glass alone (2.5% of 6–F–25 and 13–F–25) replacing a like per cent of the feldspar. It was found that the water required for a normal viscosity of the slip for lawning was only 45% for the bodies with the 6–F–25 and 13–F–25 frits and 52% for the body with 7–F–0 frit, as compared with 140% for the same body with no frit added. When portions of the slips containing the frits were allowed to stand 24 hours, they became too watery and the nonplastics separated out. This deflocculation of the slips was due to the progressive solubility of the frits.

**(2) Tests of Bodies and Ware** Two kilograms of the normal body and those containing the 6–F–25 and 7–F–0 frits were blunged in a ball mill, lawned, and de-watered on plaster. These were taken to an earthenware pottery and jiggered into 4-inch plates. The normal body was jiggered without difficulty, but those containing the frits had such poor workability that ware was jiggered with the greatest difficulty. The body with 7–F–0 frit was a little better, however, than the one containing 6–F–25.

The ware of the bodies containing frit was bisque-fired to cone 5 in a tunnel kiln, while the normal body was fired to cone 9. The ware was dipped and glost-fired as usual.

As only a few plates were made of each body, complete tests of the ware could not be made. The absorption of the fluxed ware fired to cone 5 was about 12%, while that of the normal body fired to cone 9 was 9%. The crazing resistance of the cone 5 ware was practically equal to that of the normal body fired to cone 9.

While these tests of the ware were promising, it was obvious that the use of frits in jigger bodies was impractical unless a way could be found to overcome the poor workability and to stabilize the slip.

**(3) Attempts to Stabilize the Slip** It was evident that the frit used should have a lower solubility than the 7–F–0, which was the least soluble of those studied by Collins. As this frit was otherwise promising, it was fritted with 35% feldspar to reduce the solubility. This materially reduced the deflocculating effect on the body slip since 120% of water was required (instead of 52%) for the 7–F–0 body for normal viscosity for lawning. A 50% addition of feldspar produced no better result than the 35% additions. The 7–F–35 body was still a little short and the slip became watery on aging.

Efforts were made to stabilize the slip containing the 7–F–35 glass by the use of buffer solutions and by means of slightly soluble organic acids.

NOTE: A buffer solution is a solution of a weak acid and its salt or a weak base and its salt. Such solutions resist a change in hydrogen-ion concentration with additions of acid or alkali. In the present case, a buffer solution with a hydrogen-ion concentration close to neutral would be expected to exert this buffer action and prevent a change in hydrogen-ion concentration due to the solution of the alkaline glass in the slip.

The several buffer solutions tried failed appreciably to retard the deflocculation of the slip. None of the slightly soluble organic acids avail-

NOTE: In the case of the slightly soluble acids, it was believed that one could be found which would go into solution at the same rate as the alkaline glass and which would dissociate to a degree such as to maintain a constant hydrogen-ion concentration in the slip.

able had as low a solubility as the frit. Consequently, attempts to stabilize the slip by this means were unsuccessful. It was found, however,

that hydrochloric and other acids would neutralize the slip and restore the plasticity of the body at least temporarily.

A series of body slips containing the 7–F–35 frit with additions of 0.05 to 0.20% HCl was made up and the effect of the acid on the consistency was determined with a Gardner mobilometer.[2]

The first addition of 0.05% HCl more than neutralized the slip and had a proportionately greater thickening effect than was caused by further HCl additions. On aging the slip having 0.2% HCl for 24 and 48 hours, the consistency was equivalent to a 0.15% HCl addition to the slip unaged. Similar tests with slips containing an enamel frit showed practically the same results.

From these results, and because the body containing frit with a slight excess of acid added remained as plastic as the normal body for several days, it was decided that, from the standpoint of workability, the problem of using a frit in the body was solved, since it should not be necessary to store the slip or the body more than a few days. If this were found necessary a little greater excess acid could be used.

## III. Preparing the Bodies and Making the Ware

Three bodies (150-lb. batches) were prepared in the laboratory: (1) a commercial earthenware body; (2) the same earthenware body, but with 2.7% 7–F–35 frit replacing 2.7% feldspar and 0.10% HCl added; (3) the same earthenware body, but with the addition of 3% enamel frit and 0.10% HCl.

The bodies were blunged in a small blunger, lawned, and filter-pressed. They were taken to an earthenware pottery and jiggered into 7-inch plates.

Both of the bodies containing frit were found to have the same workability as the regular body. The ware was fired in a tunnel kiln and glazed. Part of the ware of the bodies containing frit was bisque-fired at cones 5 to $6^1/_2$, while the remainder was bisque-fired to cone 9 with that of the regular body. The ware of the bodies containing frit was fired at cone 2 in the glost fire, while the ware of the regular body was glost-fired at about cone 3.

## IV. Testing the Ware

The properties of the ware as determined by tests are given in the table. The total shrinkages of the ware of the bodies containing frit fired at cones 5 and $6^1/_2$ are a little lower, while the absorptions are higher than for the regular body fired to cone 9, indicating that this ware was a little underfired but is within commercial limits. It would be necessary, however, to fire the ware of the bodies containing frit at least one cone higher (cones 6 and $7^1/_2$, respectively) or to increase the frit content of the bodies to give the ware the same shrinkage and absorption as the normal body fired at cone 9. On the other hand, the total shrinkage of the frit bodies at cone 9 is more than 1% higher than the normal body. If fired to this cone it would be necessary to have larger molds to keep within the ware-size limits.

A more serious fault, however, with the ware of the bodies containing frit is the excessive glost warpage, especially of the ware fired at the low

[2] G. H. McIntyre and J. T. Irwin, "Application of the Gardner Mobilometer to Enamel Slip Consistencies and Control," *Jour. Amer. Ceram. Soc.*, **15** [8], 433 (1932).

cones in the bisque fire. Comparative measurements of the bisque and glost warpage indicate that this warpage took place mainly in the glost fire. It is worthy of note, however, that the ware of the enamel frit body, fired at cone 9, showed no increase in warpage in the glost fire. This ware was warped but little more than that of the normal body. If this type of fluxed body be used, it will probably be necessary to use a glaze maturing at a lower cone to prevent warpage in the glost fire.

The ware of the enamel frit body (cone 9) had a lower impact value than the regular body, while its chipping value was higher. On the other hand, the impact value of the ware of the body containing 7–F–35 frit was higher and the chipping value lower than the regular body.

The crazing resistance of the ware of the body containing enamel frit, fired at cone 5, was a little lower than that of the ware of the other bodies.

TABLE I

PROPERTIES OF WARE OF COMMERCIAL EARTHENWARE BODY WITH AND WITHOUT FRIT ADDITIONS

| Body addition | Bisque cone | Total shrinkage (%) | Absorption (%) | Warpage (in.) | | Impact value (in.-lb./in.) | Chipping value (ft.-lb.) | Crazing resistance (av. failure at quench No.) |
|---|---|---|---|---|---|---|---|---|
| | | | | Bisque plates | Glazed plates | | | |
| None | 9 | 9.17 | 8.31 | | 0.08 | 4.83 | 0.06 | 10 |
| 7–F–35 frit | 6½ | 7.72 | 12.65 | | 0.12 | 7.42 | 0.02 | 10 |
| 7–F–35 frit | 9 | 10.85 | 3.61 | | 0.11 | 5.89 | 0.03 | (OK–10) |
| Enamel frit | 5 | 7.82 | 12.06 | 0.07 | 0.14 | 4.90 | 0.04 | 7 |
| Enamel frit | 9 | 10.30 | 4.03 | 0.09 | 0.09 | 3.60 | 0.07 | 10 |

## V. Conclusions

While definite conclusions regarding the use of frits in dinnerware bodies are not justified without a further study of other frits and bodies, the indications from the present study are that the advantages of using frits in an earthenware body are offset by the disadvantages.

Some practical difficulties encountered are as follows:

(1) Due to progressive solubility of the frits the slip was deflocculated and the plasticity of the bodies destroyed. These difficulties were apparently overcome by using a slight excess of hydrochloric acid in the slip.

(2) The ware of the bodies containing frit warped more than the normal body especially in the glost fire.

The only apparent advantage in the use of frit in an earthenware body would be in being able to fire the ware at a lower cone. The cost of an addition of 3% of an enamel frit such as was used in this study should be more than offset by the saving in fuel and kiln furniture.

Producing a more vitreous ware with an earthenware body containing the frits studied does not seem to be justified as this ware showed little or no improvement in properties, aside from having a lower absorption, compared with the regular ware.

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# RESISTANCE TO SUDDEN TEMPERATURE CHANGE OF SOME BODIES OF THE SYSTEM TALC–CLAY–MULLITE*

By R. M. King and C. L. Evans

ABSTRACT

Several bodies capable of being processed by the usual manufacturing methods, with varying talc, clay, and mullite content, were studied to determine their relative resistance to thermal shock. These bodies were fired at various temperatures and submitted to quenching and transverse strength tests.

## I. Introduction

Many ceramic bodies are required to have a high resistance to repeated sudden temperature change. Among the materials used to improve this property are talc, mullite, and beryl. Beryl has not come into very general use. Mullite, added as such or developed by heating clays or other aluminous silicates, is extensively used for this and other properties. For this particular property, talc is used more than is generally known and is coming into more frequent use even though it does not enjoy a good reputation among those who have had difficulty with it. Most of these difficulties, however, can be traced to the selection of an impure talc or to irregular and uneven firing conditions. A body containing both talc and clay has a short vitrification range, but this is further shortened by the presence of lime.

Note: This was found to be true by the senior author from some studies of bodies containing 50% talc which, in turn, contained 6% lime. The results of these studies have never been released for publication. Where the amount of talc added is low, the lime would not have such a deleterious effect.

With a reasonably pure talc and the more uniform firing control of modern kilns, very little trouble should be found, particularly if the body is fairly porous. It should be remembered, however, that talc seldom, if ever, has the theoretical composition of talc crystal, any more than clay has the theoretical composition of kaolinite.

## II. Items Studied

(*a*) Practical working bodies of the clay–talc–mullite system.
(*b*) Sagger bodies containing talc.

**(1) Materials** Kaolin (washed Florida kaolin).
Mullite (good commercial grade of recrystallized mullite ground to pass a 100-mesh screen).
Talc (good grade of commercial talc with an impurity content of about 2%).

**(2) Preparation of bodies** The clay-talc-mullite bodies were prepared in batches of 4000 grams by blunging and filter pressing. The sagger bodies were prepared in 5000-gram batches by dry mixing the ingredients before water was mixed therein to produce molding consistency. They were then hand-pugged and allowed to age 72 hours. All bodies were hand-pugged thoroughly before making into 1- by 1- by 4-inch bars. The firing temperatures are noted in the tables.

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* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (White Wares Division).

TABLE I

KAOLIN-TALC-MULLITE BODIES

| Body No.[a] | Fla. kaolin (%) | Talc (%) | Mullite (%) | Firing temp. | Firing shrinkage (%) | Absorption (%) | $M_1$ | $M_2$ | Reduction (%) (one quenching) | No. of quenchings |
|---|---|---|---|---|---|---|---|---|---|---|
| 11 | 60 | 40 | | 7 | 5.3 | 15.5 | 2998 | 554 | 81.8 | 2 |
| | | | | 14 | 4.3 | 14.3 | 3474 | 908 | 74.1 | 3 |
| 12 | 60 | 30 | 10 | 7 | 5.7 | 15.9 | 3230 | 366 | 88.6 | 2 |
| | | | | 14 | 4.3 | 14.9 | 3984 | 961 | 75.8 | 4 |
| 13 | 60 | 20 | 20 | 7 | 5.4 | 15.8 | 3636 | 614 | 83.2 | 3–4 |
| | | | | 14 | 4.7 | 14.4 | 4113 | 946 | 77.0 | 5 |
| 14 | 60 | 10 | 30 | 7 | 4.9 | 15.5 | 3260 | 543 | 86.3 | 3–4 |
| | | | | 14 | 5.5 | 14.3 | 3339 | 798 | 76.2 | 3–4 |
| 15 | 60 | | 40 | 7 | 5.4 | 15.3 | 3386 | 592 | 82.4 | 3–4 |
| | | | | 14 | 5.6 | 14.3 | 3203 | 705 | 77.4 | 2–3 |
| 16 | 50 | 50 | | 7 | 5.4 | 15.9 | 3520 | 1316 | 62.7 | 4–6 |
| | | | | 14 | 4.4 | 13.0 | 4026 | 1546 | 61.6 | 25+ |
| 17 | 50 | 40 | 10 | 7 | 4.4 | 15.2 | 4081 | 790 | 80.7 | 4 |
| | | | | 14 | 3.2 | 12.0 | 3932 | 1400 | 64.4 | 25+ |
| 18 | 50 | 30 | 20 | 7 | 5.4 | 15.5 | 4196 | 538 | 87.2 | 4 |
| | | | | 14 | 4.3 | 11.6 | 3337 | 1555 | 53.4 | 25+ |
| 19 | 50 | 20 | 30 | 7 | 4.3 | 14.5 | 3868 | 533 | 86.2 | 4 |
| | | | | 14 | 4.2 | 11.5 | 4024 | 1598 | 60.4 | 25+ |
| 20 | 50 | 10 | 40 | 7 | 4.3 | 15.9 | 2712 | 767 | 79.8 | 4–5 |
| | | | | 14 | 7.5 | 11.5 | 3439 | 822 | 76.7 | 4–5 |
| 21 | 50 | | 50 | 7 | 3.6 | 14.7 | 4090 | 841 | 79.5 | 3–4 |
| | | | | 14 | 3.8 | 13.3 | 4507 | 734 | 83.7 | 2–3 |
| 22 | 40 | 60 | | 7–8 | 3.8 | 18.0 | 3810 | 754 | 80.2 | 5 |
| | | | | 13–14 | 6.9 | 2.6 | 7084 | 1370 | 73.1 | 10 |
| 23 | 40 | 50 | 10 | 7–8 | 4.1 | 14.0 | 4277 | 1242 | 70.9 | 10 |
| | | | | 13–14 | 5.5 | 8.5 | 5294 | 1396 | 73.6 | 17 |
| 24 | 40 | 40 | 20 | 7–8 | 3.3 | 13.8 | 4696 | 1185 | 74.8 | 13 |
| | | | | 13–14 | 3.3 | 14.5 | 5284 | 1309 | 75.3 | 18 |
| 25 | 40 | 30 | 30 | 7–8 | 3.7 | 14.6 | 3630 | 830 | 77.2 | 3 |
| | | | | 13–14 | 3.7 | 13.0 | 5072 | 969 | 80.9 | 11 |
| 29 | 30 | 70 | | 7–8 | 4.0 | 16.0 | 4806 | 318 | 95.4 | 1 |
| | | | | 13–14 | fused | | | | | |
| 30 | 30 | 60 | 10 | 7–8 | 3.3 | 16.5 | 4098 | 544 | 86.9 | 2 |
| | | | | 13–14 | 3.3 | 14.0 | 4910 | 1065 | 78.3 | 12 |
| 31 | 30 | 50 | 20 | 7–8 | 3.3 | 15.3 | 4185 | 909 | 78.2 | 3 |
| | | | | 13–14 | 4.3 | 10.0 | 6296 | 1388 | 78.0 | 15 |
| 32 | 30 | 40 | 30 | 7–8 | 3.3 | 15.4 | 4815 | 1007 | 78.9 | 2 |
| | | | | 13–14 | 3.0 | 12.6 | 4714 | 1028 | 78.1 | 11 |

[a] These numbers refer to corresponding members of a triaxial study of Florida kaolin (top), talc (lower left), and mullite (lower right).

TABLE II

SAGGER BODY STUDY

(Firing temperature, cones 9–10)

| Body No. | Sagger ball clay (%) | Plastic fire clay (%) | Grog 40–80 mesh (%) | Talc (%) | Firing shrinkage (%) | Absorption (%) | $M_1$ | $M_2$ | Reduction (%) (one quenching) | No. of quenchings |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 48.75 | 16.25 | 35.00 | | 4.2 | 13.5 | 2702 | 650 | 75.8 | 5 |
| 2 | 46.31 | 15.44 | 33.25 | 5.0 | 4.7 | 11.0 | 3110 | 633 | 79.6 | 6 |
| 3 | 43.87 | 14.63 | 31.50 | 10.0 | 4.2 | 10.8 | 3380 | 768 | 77.3 | 10 |
| 4 | 41.44 | 13.81 | 29.75 | 15.0 | 4.2 | 10.5 | 3314 | 926 | 72.1 | 13 |
| 5 | 39.00 | 13.0 | 28.0 | 20.0 | 4.2 | 10.4 | 3030 | 985 | 67.5 | 25+ |

## III. Tests

(1) Linear firing shrinkage (10 bars).
(2) Absorption (3 half-bars).
(3) Fired modulus of rupture (10 bars).
(4) Modulus of rupture after one quenching (10 bars).
(5) Number of quenchings up to 25 (10 bars).

All quenching tests were carried out from 1600°F to room temperature in water, until the bars could be broken with the fingers.

All measurements and calculations were carried out according to American Ceramic Society Standard Methods with the exception of linear firing shrinkage and "per cent reduction." The customary procedure was followed in determining linear shrinkage directly. "Per cent reduction" was obtained as follows:

$$\frac{M_1 - M_2}{M_1} \times 100 = \% \text{ reduction}$$

$M_1$ = original modulus of rupture
$M_2$ = modulus of rupture after one quenching

## IV. Results

The preceding tables give the results obtained. A microscopic examination was made of body 23, which showed the development of the mineral cordierite and an isotropic glass of high MgO content. Enstatite, which has been reported[1] as a constituent of fired talc bodies, was not found.

## V. General Conclusions

When firing temperature was sufficient to cause appreciable vitrification, talc bodies showed high resistance to thermal shock and lowered reduction of modulus of rupture after quenching with increased talc content.

When talc was added in increasing amounts up to 20% to a typical sagger body, resistance to thermal shock was markedly increased and reduction in strength was gradually decreased.

Microscopic examination of body No. 23 showed development of crystalline cordierite and a high magnesia glass.

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[1] Rieke and Thurnauer, "Effect of Talc Additions on Firing Behavior and Some Technically Important Properties of Pure Kaolin," *Ber. deut. keram. Ges.*, **13** [6], 245–53 (1932).

# HIGH-TEMPERATURE PREPARATION AND THE OPTICAL PROPERTIES OF SODIUM ALUMINATE*

By K. Kammermeyer† and Albert B. Peck‡

ABSTRACT

Crystalline sodium aluminate was prepared by heating monomolecular and other mixtures of $Na_2CO_3$ and $Al_2O_3 \cdot 3H_2O$ for varying periods to temperatures up to 1700°C.

The constituents produced were identified by petrographic-microscopic methods, and new optical data on sodium aluminate was obtained.

Sodium aluminate was found to exist from temperatures below 1100 to above 1700°C, its melting point being above 1700°C.

Small amounts of iron oxide aid the formation of sodium aluminate, especially at the lower temperatures.

## I. Introduction

Since attention has recently been called by Carter and King[1] to the use of sodium aluminate as an electrolyte in casting slips, some additional data on its preparation and optical properties may be of interest to ceramists.

The literature which deals with the preparation of sodium aluminate from soda and alumina at temperatures above 1200 to 1300°C is limited. Most references deal with temperatures below 1000°C, and some involve experiments between 1000°C and 1300°C.

Matignon[2] in 1920 was probably the first investigator to give special attention to sodium aluminate, since he became interested in it as a possible refractory material. His name is familiar in the literature through his determination of the melting point of the compound which he found to be 1650°C by optical pyrometer methods. His statement, however, that sodium aluminate forms between 1100°C and 1200°C when an intimate mixture of $Na_2CO_3$ and $Al_2O_3$ is heated in monomolecular proportions had already been anticipated in 1910 by J. W. Cobb,[3] who stated that complete reaction between soda and alumina takes place at 1150°C. According to Cobb's results, evolution of $CO_2$ from a mixture of the two compounds began at about 700°C, and he placed the temperature of incipient formation of sodium aluminate at 720°C. In 1926, G. Feld[4] placed the temperature of the complete reaction at 950°C.

It is significant that none of these investigators attempted to prove the existence of the compound $Na_2O \cdot Al_2O_3$ by observation of its crystalline state. All investigators on the subject previous to 1932 took it for granted that water-soluble alumina was equivalent to the existence of a compound. Only with the appearance of a publication by L. T. Brownmiller and R. H. Bogue[5] in 1932 was it definitely established that the compound $Na_2O \cdot Al_2O_3$ exists, the optical properties of which were reported at the same time.

The present investigation had as its object the preparation of sodium aluminate at temperatures near its reported melting point and the deter-

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[1] *Jour. Amer. Ceram. Soc.*, **15** [8], 407–409 (1932).

[2] Matignon, *Compt. rend.*, **177** [24], 1290 (1920).

[3] J. W. Cobb, *Jour. Soc. Chem. Ind.*, **29**, 399 (1910).

[4] G. Feld, *Z. angew. Chem.*, **39**, 174 (1926).

[5] L. T. Brownmiller and R. H. Bogue, "The System CaO–$Na_2O$–$Al_2O_3$," Bur. Stand., Portland Cement Assn. Fellowship, Paper No. 25, p. 508.

mination of the optical properties of the compound. It was also hoped to obtain at least approximate data on the melting point of the compound.

## II. Equipment

The firing of the samples was carried out in a small gas-fired furnace having a primary combustion space of about 18 cubic inches. The gases of combustion were directed downward along the wall of the primary combustion space before reaching the flue. This construction enabled a temperature of 1600°C with gas and unpreheated air to be reached. Temperatures up to 1720°C were obtained by the use of gas and oxygen.

The temperatures were measured by means of a platinum platinum-rhodium thermocouple, which for high-temperature measurements was calibrated frequently against the melting point of its platinum wire, while the usual calibrating procedure was used for the lower temperature measurements. The couple projected into the furnace through the top, and the bead was protected from direct contact with the flame by a platinum foil shell.

The samples to be fired were enclosed in a platinum foil capsule which was supported on the thermocouple protecting tube by means of platinum wire. The capsules were located next to the thermocouple bead to obtain their temperature as closely as possible. It was estimated that the recorded temperatures did not vary more than ±20°C from the temperatures of the samples. The temperature to which the samples could be heated was limited by the use of platinum, whose melting point is 1755°C.

After exposure to the desired temperature the samples were cooled slowly in order to promote the formation of crystals sufficiently large for microscopic examination.

The raw materials used for the samples were $Al_2O_3 \cdot 3H_2O$ and anhydrous $Na_2CO_3$ in finely powdered condition. The samples were prepared by proportioning the raw materials in the desired ratio, followed by thorough mixing before charging into the capsules.

## III. Experiments

A considerable number of experiments were conducted before a satisfactory technique could be developed by which the nine samples, reported in the following section, were prepared.

In two samples an excess of $Na_2O$ was used to counteract the volatilization of soda which is appreciable at elevated temperatures. All other samples were made up in monomolecular proportions. Two of these samples contained about 3.5% by weight of iron oxide and represented duplicate runs of two other samples without iron oxide addition.

A summary of the experimental results is presented in Table I which contains the ratios of $Na_2O$ to $Al_2O_3$ in the raw mixes, the maximum temperatures recorded, the condition of each sample after firing, the total time of firing, the time for which the samples were exposed to temperatures above 1600°C for the high-temperature runs, and the time of exposure above 1100°C for the low-temperature runs. The last two items were used as a comparative criterion for duplicate runs.

From this table it is seen that samples 4 and 7 and samples 6 and 8 represent duplicate runs at high and low temperatures, respectively, the only difference being the addition of iron oxide in samples 7 and 8.

All samples were submitted to petrographic-microscopic examination by the powder immersion method and the optical properties of the compounds formed were determined. Positive identification of a crystalline compound was possible in all cases, but only samples 2, 3, 4, and 7 permitted the determination of the refractive indices and of the optic angle. The optic angle was measured by means of an "optic angle diaphragm objective."[6] Table II contains the results of the microscopic examination, and gives the reported values for comparison.

The runs at 1100°C and 1200°C were made with the object of attempting to identify crystalline sodium aluminate in the samples, which would confirm the view held by previous investigators that the compound formed at these temperatures. Although the crystalline development was too fine to permit determination of all three indices, it was apparent that a doubly refracting crystalline compound had been formed which had an average index close to 1.580. Since this corresponds to the average of the refractive indices of $Na_2O \cdot Al_2O_3$ as determined upon well crystallized material, it seems practically certain that this compound forms to some degree at the temperatures indicated and that with longer heating it might be produced at still lower temperatures. This compound appeared to act as a binding material between grains of uncombined alumina.

Some samples fired at high temperatures showed varying amounts of finely fibrous aggregates which appeared to be excess alumina in the form of the beta modification. Sample 1 did not show complete combination and its crystalline development was still too fine to permit detailed determination of indices. Sample 2, although made up with 25% excess $Na_2O$, showed some excess $Al_2O_3$, probably due to the high temperature and long period of heating resulting in considerable volatilization of $Na_2O$. Sample 4 showed the greatest excess of $Al_2O_3$, as was to be expected, since it was made up in a monomolecular ratio and was exposed approximately to the same conditions

TABLE I

SUMMARY OF EXPERIMENTAL DATA

| Sample No. | Molecular ratio $Na_2O/Al_2O_3$ | Maximum temp. (°C) | Condition of sample | Total firing time | Time above 1600°C | Time above 1100°C | Remarks |
|---|---|---|---|---|---|---|---|
| 1 | 1.25:1 | 1563 | Not sintered | 15 hr. | | | |
| 2 | 1.25:1 | 1715 | Sintered | 7 hr. 30 min. | 2 hr. 25 min. | | |
| 3 | 1:1 | 1667 | " | 5 hr. | 15 min. | | |
| 4 | 1:1 | 1700 | Well sintered | 6 hr. | 2 hr. | | |
| 5 | 1:1 | 1232 | Not sintered | 2 hr. 40 min. | | 2 hr. | |
| 6 | 1:1 | 1216 | " | 9 hr. 25 min. | | 8 hr. 15 min. | |
| 7 | 1:1 | 1720 | Very well sintered | 4 hr. | 2 hr. | | 3.5% $Fe_2O_3$ |
| 8 | 1:1 | 1231 | Not sintered | 10 hr. | | 7 hr. 50 min. | 3.5% $Fe_2O_3$ |

[6] This objective was recently devised by C. B. Slawson and carries a variable iris diaphragm which, by proper calibration, enables a direct reading of the optic axial angle to be obtained.

as sample 2. Samples 3 and 7 showed only small amounts of excess $Al_2O_3$.

A comparison between the duplicate runs with and without addition of iron oxide showed definite evidence that the addition of iron oxide had a beneficial influence upon the combination of $Al_2O_3$ and $Na_2O$. In sample 8, fired at 1100 to 1200°C, a much greater combination of $Al_2O_3$ was apparent than in sample 6, and furthermore, the size of the sodium aluminate crystals which were formed was considerably improved. Samples 4 and 7 differed mainly in regard to the size of the crystals, the additional iron oxide in sample 7 giving definitely larger crystals than in sample 4. There also seemed to be a slight decrease in the amount of excess $Al_2O_3$ in the case of sample 7.

None of the samples showed any signs of actual fusion, although samples 2, 4, and 7 were well sintered. Sample 7 was very well sintered, probably due to the presence of iron oxide which would tend to lower the melting point. Consequently, it appears that the melting point of sodium aluminate is above 1700°C. The highest temperature measured was 1720°C in the firing of sample 7. Since, however, at such high temperatures it appears quite probable that a difference of as much as 20°C may exist between the thermocouple and the sample, a minimum temperature of 1700°C seems reasonable.

TABLE II

OPTICAL PROPERTIES OF SODIUM ALUMINATE

Occurs generally in irregular to equant grains, occasionally nearly square in cross-section.

Biaxial and negative

| | | Found | Reported[5] |
|---|---|---|---|
| Indices of refraction | alpha | 1.567 ± 0.003 | 1.566 ± 0.003 |
| | beta | 1.581 ± 0.003 | 1.575 ± 0.003 |
| | gamma | 1.584 ± 0.003 | 1.580 ± 0.003 |
| Axial angle | 2 V | 38° | 30° |

Twinning is sometimes present but does not appear to be a constant characteristic. A good cleavage often appears in two directions, nearly at right angles. There are some indications of a third cleavage.

## IV. Conclusions

(1) Sodium aluminate ($Na_2O \cdot Al_2O_3$) was identified in $Na_2CO_3$–$Al_2O_3$ firings and its optical properties were determined. As shown in Table II the optical properties agree fairly well with those of Brownmiller and Bogue.

(2) Sodium aluminate was found to exist in crystalline form in samples heated at 1100 to 1200°C, confirming the conclusions of previous investigators which were based upon the presence of water-soluble alumina.

(3) The melting point of sodium aluminate was found to lie above 1700°C, agreeing with the work of Brownmiller and Bogue who found no evidence of melting at 1650°C.

(4) The presence of about 3.5% by weight of iron oxide had a beneficial influence upon the formation of sodium aluminate, especially at the lower temperatures.

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# THE RELEASE OF STRAIN IN GLASS*

By James Bailey and Donald E. Sharp

ABSTRACT

Measurements of strain release[1] showed that check results were obtained only when the previous history of the samples was the same. Moreover, it was found that the release of strain was more rapid at first than could be accounted for by the equation of Adams and Williamson.

This paper discusses the effect of previous history on the measurements, describes an improved device for loading the specimens, and suggests a logarithmic equation which, in general, fits the observations better than that of Adams and Williamson. Tests of the equation are made both on data obtained from the modified apparatus described and on the data of Adams and Williamson. It is indicated that the Adams and Williamson equation gives too long an annealing time at higher temperatures and too short an annealing time at lower temperatures.

It appears that the rate of release of strain depends on some power of the strain which varies from unity at high temperatures where the glass is a viscous fluid to a higher power at low temperatures where the release of strain is elastico-viscous in character. With a single specimen at any fixed temperature in the annealing range, however, it appears that the release of strain in various parts of the specimen takes place at a rate which is proportional to the strain, but that the rate undergoes continual change with time.

## I. Introduction

Further experiments with the apparatus described in a previous paper[1] indicated that certain anomalous behavior took place during the release of strain in a glass sample subjected to mechanical loading. The observed release of strain was too rapid at first,[2] and the curves obtained by experiment did not strictly follow the curve[3] computed by the use of the equation of Adams and Williamson.[4] These phenomena seemed worthy of further study, and to this end a rather extended series of experiments was conducted using much larger slabs of optical glass and a slight modification of the loading apparatus. The present paper deals with some of the results of these experiments together with data and certain equations which seem to fit the strain-time curves more closely than those formerly used. Possible errors due to the type of apparatus used were investigated and the results are reported herein.

## II. Effect of Previous History

It was apparent at once with the larger slabs of optical glass that some peculiar change in the rate of release of stress took place as the elapsed time became greater. Moreover, repeat tests on a sample at the same temperature, made by retightening the pressure screw, gave quite different curves than those obtained originally on the annealed sample. The differences were so marked that it was obvious that equations derived from the

* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (Glass Division). Received May 4, 1933.

[1] D. E. Sharp, James Bailey, and I. Hyman, *Jour. Amer. Ceram. Soc.*, **14** [11], 820–26 (1931).

[2] *Ibid.*, p. 822. Corrections to this paper should be made as follows: Birefringence should always be figured in mμ per cm. before applying the readings to the formula. Fig. 4 should be corrected as follows: Ordinates should read "Time of Release of Strain from 150mμ to 50mμ." In Fig. 5, the ordinates should read "Birefringence in mμ per cm."

[3] *Ibid.*, Fig. 5, p. 825.

[4] L. H. Adams and E. D. Williamson, *Jour. Franklin Inst.*, **190**, 597–631, 835–70 (1920)

curve of first release could not be used for computation along any other curve subsequently obtained on the same sample of glass. Repeat curves of the same nature could only be obtained after careful annealing. It was quite evident that the past history must be considered when annealing data are being obtained by this method.

Berger[5] has pointed out the effect of past history on many of the physical properties of glass. Moreover it has been known for some time that the previous history of the sample has an effect upon its birefringence under load.[6] Filon and Harris noted that the black line seen in a Babinet compensator did not return to zero after removal of the load from a block of glass which had been loaded during forty-two hours of annealing and subsequent cooling. The black line remained in the same direction as that caused by the load and was of the same sign throughout the cross-section.

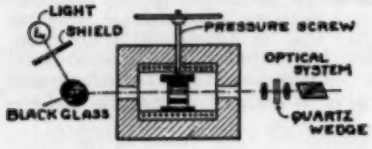



FIG. 1.

A similar experiment was repeated in this laboratory on a slab loaded with a bending stress and a similar phenomenon was observed. The residual birefringence, however, was entirely too small to be the prime cause of the decrease in rate of release of strain observed in these experiments under repeated loadings.[7]

Other experiments were conducted on blocks of glass sufficiently loaded by weights to cause a birefringence of approximately 30 mμ per centimeter. These were held at constant temperature under load for five to six hours during which time no change in the observed birefringence greater than the experimental error could be observed. It seems quite certain, therefore, that the apparent change in the rate of release of stress can not be due to a change in the stress-optical coefficient.

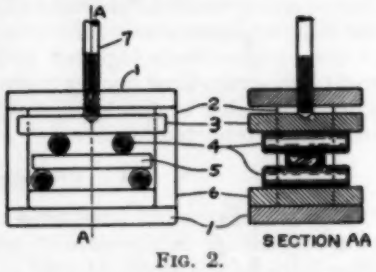



FIG. 2.

The effects of temperature and time on the photoelastic constant are discussed by Coker and Filon.[8] From their work the indications are that the change in birefringence with time for constant stress is negligible over the period of time used in the present experiments. It seems likely, however, that the stress-strain relation will change slightly with a long elapsed time at the annealing temperature.

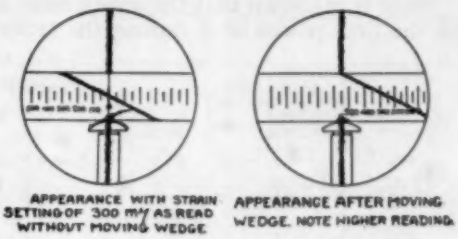
## III. Apparatus

The apparatus (Fig. 1) consisted of an electric furnace, the temperature of which was accurately controlled. A beam of polarized light passed through a hole in one end of the furnace and thence consecutively through the glass sample, a hole in the furnace door, an objective, a quartz wedge,

[5] E. Berger, *Jour. Amer. Ceram. Soc.*, **15**, 647–77 (1932).
[6] L. N. G. Filon and F. C. Harris, *Proc. Roy. Soc.* [London], **103** [Series A], 561.
[7] The birefringence of glass under various conditions is well discussed by Harris in "The Photoelastic Properties of Glass," *Jour. Soc. Glass Tech.*, **13**, 213–19 (1929).
[8] E. G. Coker and L. N. G. Filon, Photo-Elasticity, Cambridge Press, 1931.

the eyepiece, and a nicol prism. The lens system gave an enlarged view of the sample. The apparatus was identical with that described in a former paper[9] except that the glass samples were much larger and were loaded by a system of rollers so that end pressures were avoided.

The metal loading frame is shown in Fig. 2 with the pressure screw, 7, which extended outside the furnace. The thrust was transmitted through the top piece, 1, and the two side pieces, 2, to the bottom plate, 1. On this plate rested the roller plate, 6, which could easily be removed and polished. The rollers, 4, supported the glass, 5. The two bottom rollers were as near the ends of the slab as possible while the two upper rollers were spaced nearer the center as shown. The rollers were $^3/_8$ inch in diameter and extended well out beyond the glass so that they were sure to have full bearing across the section. The piece, 3, rested on the upper rollers and was guided by the sides, 3. The glass samples used in the experiments were approximately 2 inches long, $^3/_4$ inch wide, and from $^3/_{16}$ to $^5/_{16}$ inch thick. To apply the load, the screw, 7, was turned down until the desired birefringence was observed.


APPEARANCE WITH STRAIN SETTING OF 300 mμ AS READ WITHOUT MOVING WEDGE
APPEARANCE AFTER MOVING WEDGE. NOTE HIGHER READING
A
B

FIGS. 3A AND 3B.

At the same time that a specimen is loaded the iron parts are also put under stress and, of course, some of the strain removed by viscous flow of the glass has its origin in the deflection of the metal parts. The relative elastic deformation due to this pressure has been computed and it was found that only a very small percentage of the deformation is due to the metal parts. Moreover, repeated measurements show that the metal does not permanently change its shape under stress. The error caused by stressing the metal parts is therefore negligible and is constant for any specimen. It should be remembered that the difference in thermal expansion between the glass and metal does not affect the results since the temperature is constant. With the improved method of loading the specimen, the central region has a uniform bending moment, and disturbing local pressures under the rollers are not present along the line, $AA$, of observation (Fig. 2).

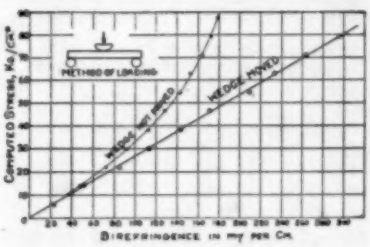



FIG. 4.

NOTE: Readings taken with the central loading, as used in the former apparatus, caused some irregularity near the bearing of the saddle at the end of the pressure screw, although in general these disappeared before the tension side was reached. A view of a loaded specimen as it appeared in the older apparatus is shown in Fig. 3A. The black line was sensibly straight but a curved "tail" usually ran from the contact line under the

[9] See footnote 1.

screw to meet the other line and confused the readings along the compression surface as shown. The chief difficulty with this method was that the bending moment changed from a maximum at the center to zero at the end supports and a reading on the scale of the quartz wedge as shown in Fig. 3A appeared much too small. Measurements should always be taken by sliding the wedge as in Fig. 3B. Even with the roller method of loading (Fig. 2), better results are obtained by moving the wedge, and indeed this must be done when high stresses are being used. The error which may result by reading the black line on the scale of the wedge without moving the wedge is shown in Fig. 4.

Since it is known that the strain must relieve itself at a rate proportional to the first power of $S$ during the truly viscous high-temperature range

TABLE I

| Temp. | Ref. No. | Page | Equation |
|---|---|---|---|
| 480 | 1 | 613 | Log (T + 150) = −2.35 log $S$ + 7.93 |
| 500 | 2 | " | " (T + 50) = −1.45 " " + 5.57 |
| 530 | 3 | " | " (T + 30) = −0.753 " " + 3.273 |
| 450 | 4 | " | " (T + 500) = −1.014 " " + 5.448 |
| 470 | 5 | " | " (T + 90) = −1.267 " " + 5.12 |
| 490 | 6 | " | " (T + 30) = −1.948 " " + 6.08 |
| 500 | 7 | " | " (T + 400) = −0.271 " " + 3.171 |
| 515 | 8 | " | " (T + 2) = −2.422 " " + 6.97 |
| 500 | 9 | " | " (T + 50) = −1.653 " " + 6.432 |
| 516 | 10 | " | " (T + 110) = −0.848 " " + 4.25 |
| 540 | 11 | " | not enough points |
| 540 | 12 | " | " (T + 100) = −1.75 " " + 6.94 |
| 565 | 13 | 614 | " (T + 90) = −0.788 " " + 4.06 |
| 590 | 14 | " | " (T + 25) = −0.752 " " + 3.02 |
| 450 | 15 | " | " (T + 100) = −0.961 " " + 4.581 |
| 470 | 16 | " | " (T + 95) = −0.437 " " + 3.058 |
| 490 | 17 | " | " (T + 10) = −1.537 " " + 4.368 |
| 385 | 18 | " | " (T + 20) = −1.265 " " + 4.605 |
| 400 | 19 | " | " (T + 50) = −0.570 " " + 3.096 |
| 415 | 20 | " | " (T + 15) = −0.618 " " + 2.715 |
| 306 | 21 | " | " (T + 6000) = −2.367 " " + 9.817 |
| 374 | 22 | " | " (T + 60) = −1.670 " " + 6.426 |
| 390 | 23 | " | " (T + 40) = −1.040 " " + 4.472 |
| 406 | 24 | 615 | " (T + 25) = −0.943 " " + 3.758 |

NOTE: $S$ in the above table corresponds to $\delta$, the optical path difference of the data of A. and W. If $S'$ is the birefringence in m$\mu$ per cm. and $l$ is the length of the optical path, then $S = lS'$. The equations have been worked out using the observed birefringence in order that the results may be directly compared to the data as given. In general the observations should be reduced to m$\mu$ per cm. before working out the constants of the equation.

of molten glass, and since it has been found that the release of strain in the low-temperature range (Fig. 6) may be quite accurately represented by an equation having $S$ raised to the 3.2 power, it might be inferred that the rate of release of strain is a function of the temperature and varies from the first power to some other higher power as the temperature diminishes. Moreover, when measurements of release of strain are made, the time readings may have been started at any arbitrary time, but the past history nevertheless will affect the curve in some manner.

Both of these assumptions may, to some extent, be incorporated in an equation having the form

$$\log (T + A) = m \log S + K \tag{1}$$

where $A$, $m$, and $K$ are constants.

The flexibility of this equation makes it adaptable to the mathematical representation of a much wider series of curves than would be possible if the power of $S$ were fixed. In general, it has been possible to fit this formula reasonably well to the data thus far taken. The formula, however, can not in all cases be made to represent accurately the rapid release of strain which occurs during the first few minutes after reapplying the load.

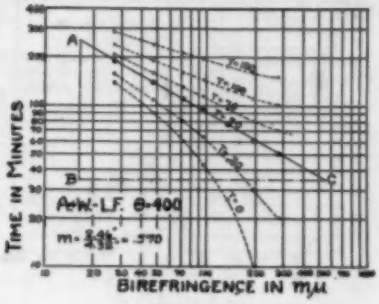



FIG. 5.

## IV. Test of Equation 1 on Data of Adams and Williamson

Since the present method stresses the sample in a manner that is not strictly analogous to a cooling stress, it was thought advisable to test equation (1) with some of the data of Adams and Williamson. Table I shows the logarithmic equations derived from some of the Adams and Williamson data by assuming values for $A$ and obtaining the constant, $m$, by graphical methods. Since the values of $m$ and $K$ are influenced by the value of $A$, which is determined empirically, all of these constants may vary perhaps 10%, but they are definite for particular values of $A$. The constant, $K$, is obtained by substitution from the data. Computations were made on the slide rule and the values given here are subject to the slight errors from such a source.

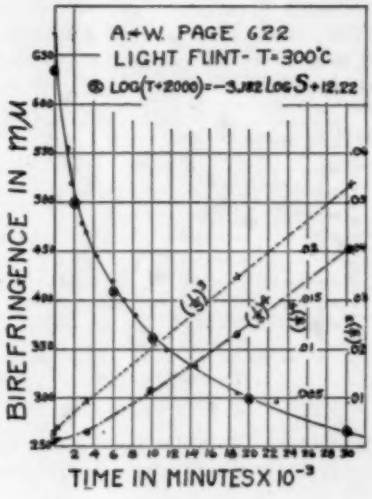



FIG. 6.

It can be seen that in general the value of $m$ is numerically larger at low temperatures and tends to grow smaller for the higher temperatures. Likewise the value of $A$ tends to be large for the low temperatures and small for the high temperatures. Although the "ordinary crown" (groups Nos. 4 to 8 inclusive) does not show this arrangement and No. 17 seems to be out of order, the results as a whole seem to agree with the hypothesis that $m$ may vary from zero for truly viscous glass at high temperatures to a very high value at room temperature.

Equation 1 may be reduced as follows by letting $K = \log P$:

$$\text{Log } (T + A) = m \log S + K \tag{1}$$

$$\frac{(T+A)}{P} = S^m \qquad (2)$$

Differentiating,

$$\frac{dS}{dT} = \frac{S^{1-m}}{R}$$

When $m$ works out to be a negative number, as in the equations in Table I, the rate of release of strain is equal to unity plus the numerical value of $m$. It may therefore be stated that the apparent rate of release of strain varies from unity during the viscous state of glass to a high power at a low temperature.

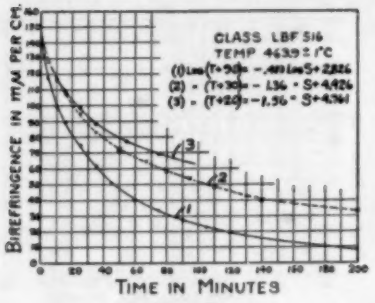


FIG. 7.

The constant, $A$, depends chiefly upon the rapidity of the release of strain during the first few observations. When the initial rate of release is large, $A$ will also be large, and consequently $m$ will be small.

This interdependence of the constants can best be understood by referring to Fig. 5 which shows the method of deriving the constants $A$ and $m$ graphically. In this figure, time is plotted as ordinate and mμ or $S$ as abscissa on double log paper, and it is to be noted that the points fall on a curve concave toward the origin. If various values of $A$ are assumed and plotted, the line tends to straighten out as $A$ becomes greater. Thus $T + 0$ is decidedly curved, $T + 20$ is straighter, and $T + 50$ is approximately a straight line. $T + 70$, $T + 100$, and $T + 150$ are curved in the opposite direction. In the case of Adams and Williamson L. F. ($\theta$ = 400°C), the line $T + 50$ represents the data fairly well. Drawing the best straight line, $AC$, through the points, and drawing the line, $AB$, parallel to the time ordinate and $BC$ parallel to the strain abscissa gives the right triangle $ABC$. $AB$ and $BC$ should be measured in inches. The quotient of $AB$ divided by $BC$ gives $m$. $K$ may be determined by reading any value of $(T + A)$ and the corresponding value of the strain and by substituting in the equation. It should be noted that the line, $AB$ (extended if necessary), enables the values of $(T + A)$ and $S$ to be read directly for any time or strain desired without any computation.

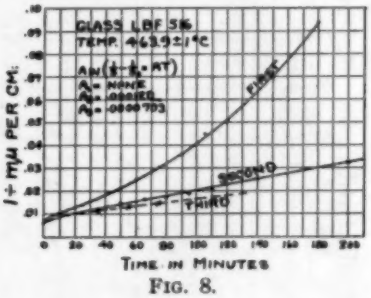


FIG. 8.

Figure 6 shows[10] how well the log formula fits these data. Incidentally, it shows that $A$ is large and that $m$ also is large for this low temperature and slow release of strain. The reciprocals of $S^3$ and $S^4$ are also plotted in this figure, and are curved in opposite directions, showing that the rate of release of strain in this case is between the fourth and fifth power of $S$

[10] Adams and Williamson, *loc. cit.*, p. 622.

instead of the square of $S$ as required by the Adams and Williamson equation (equation (3) this paper).

## V. Test of Equations 1 and 2 on Data of Bailey and Sharp

Figure 7 shows the strain-release curves due to repeated mechanical stressing in the apparatus described at the beginning of the present paper. The strain-release measurements were made on slabs of light barium flint glass held at a constant temperature of 464°C. The constants of the log equation are given. While these constants progress in a systematic manner from one curve to the other, too much physical significance must not be placed on this change in value. The important thing is that each curve leads to an entirely different value of strain for any elapsed time.

Figure 8 shows these curves plotted $1/S$ against time according to the method of Adams and Williamson. The first curve can not give a value for $A$ in the equation

$$\frac{1}{S} - \frac{1}{S_0} = AT \qquad (3)$$

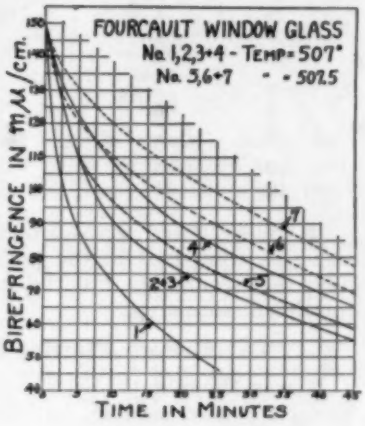



FIG. 9.

The second and third curves are straight enough so that they can be used to determine the value of $A$, but the third curve gives a value of only about one-half that of the second curve. The great effect of the previous history on the annealing time is thus apparent.

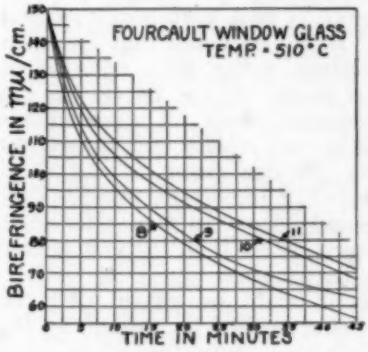



FIG. 10A.

Figures 9 and 10A show a nest of repeat curves on a good sample of Fourcault sheet window glass. The first curve is decidedly lower than the others. The second and third for some unknown reason fall almost on top of one another. The fourth is decidedly higher than these.

Curves 5, 6, and 7 were taken after the lapse of perhaps fifteen minutes during which the temperature rose a half degree. Due, probably, more to the time between readings than to the higher temperature, curve 5 is below curve 4, but curves 6 and 7 are higher in the order named.

Curves 8 and 11 in Fig. 10A were made on the same specimen without disturbing the apparatus. The furnace, however, had been cooled off and then raised to a temperature of approximately 530°C for one hour after which it was lowered to 510°C and allowed to become constant before starting the experiment. Curve 8 matches curve 4 quite closely and curve

11 is between curves 6 and 7 of Fig. 9. It should be noted that a reasonably good annealing and an increase of temperature of 3°C did not reduce the annealing time to that indicated by the first curve of release of strain for this glass.

The log equations for these curves have been computed for comparison and are given in Table II.

TABLE II

| Fig. No. | Curve No. | | Temp. |
|---|---|---|---|
| 9 | 1 | $\text{Log}(T+2) = -2.38 \log S + 5.476$ | 507°C |
| 9 | 2, 3 | $"(T+5) = -2.375 " " + 5.853$ | |
| 9 | 4 | $"(T+10) = -2.07 " " + 5.502$ | |
| 9 | 5 | $"(T+5) = -2.54 " " + 6.23$ | 507.5°C |
| 9 | 6 | $"(T+10) = -2.33 " " + 6.068$ | |
| 9 | 7 | $"(T+15) = -2.345 " " + 6.276$ | |
| 10 | 8 | $"(T+7) = -2.075 " " + 5.362$ | 510°C |
| 10 | 11 | $"(T+10) = -2.36 " " + 6.126$ | |

It will be noted that all of the constants are relatively near the same value as compared to the rather wide range of values shown in Fig. 7. This fact seems odd, but the authors are not prepared to offer any reason for this dissimilarity.

## VI. Factors Affecting Character of Strain-Release Curves

It was thought that different types of glass might behave differently under repeated loading, but the increase in the height of the curves was found to persist with every type of glass tried. Figure 11 shows a nest of four curves obtained by repeated straining of a dense flint glass.

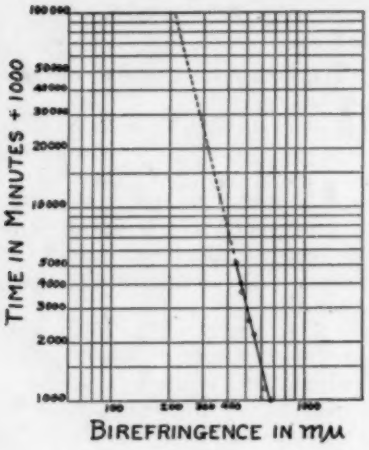



FIG. 10B.

Figure 12 shows the curves obtained on an alkali-free glass made by fusing commercially pure barium silicate and $B_2O_3$. It will be noted that the glass will become softer with addition of $B_2O_3$ as shown by the curves on the first release of strain. The same holds for the second release and apparently also for the one curve of the third release. The important thing is that the second release on the softer glass was much slower than the first release on the harder glass.

Since it might be argued that the above effect could be caused by the roller sinking into the glass, thus increasing the contact area and reducing the rate that the rollers sink into the glass, a series of experiments was tried using blocks of glass loaded on the ends as shown in Fig. 13. Exactly the same slowing down of the rate of release under loadings was noted.

Since most of the efforts of the writers were spent in endeavoring to discover some connection between the behavior of the sample during the

release of strain and its past history, successive experiments on samples of the same glass having the same past history at a series of widely varying temperatures were neglected. Only by this means can the relationship between the temperature and the constants be determined. Thus far the experiments indicate that $m$ is numerically smaller when the temperature is high, but definite data can not be given because the past heat treatment has not usually been well enough known.

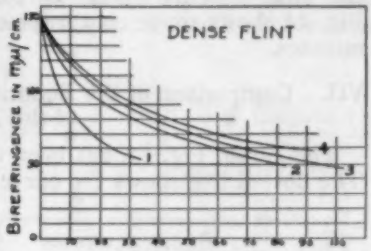


FIG. 11.

It should be remarked that smooth curves of the rate of release of strain are not easy to obtain. Since the rate of release of strain changes very rapidly with temperature and the errors are accumulated, the slightest temperature change causes a marked irregularity of the curve.

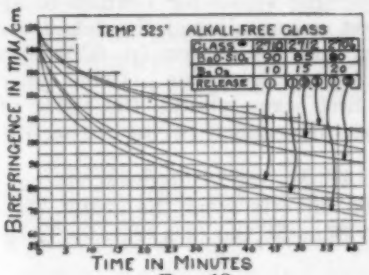


FIG. 12.

In many cases when the results were plotted a decided wave was found in the part of the curve between the rapid release at the start and the flatter portion near the bottom. In several cases this wave appeared in all of the release curves on the same sample. It may be that this peculiar behavior is due to some sort of error which the writers were unable to detect.

If the curves (Figs. 9 and 10A) are critically examined it can be noted that both the upper and lower ends seem too straight. It appears that a greater change in the rate of release between the time interval, five minutes to fifteen minutes, is taking place than at any other part of the curves.[11] The observations which gave the above curves were continued for 45 minutes which, in terms of the long time used in annealing optical glass, would be considered as the very first few minutes. They therefore represent, for the most part, that portion of the curve which departs from the formula of Adams and Williamson. In commercial annealing, however, the entire time in the leer is usually less than two hours and the period of time for the release of strain would not usually exceed 45 minutes. In this respect the curves (Figs. 9 and 10A) are practicable, but the writers would hesitate to use the derived equation for extrapolation too far along the elapsed time coördinate.

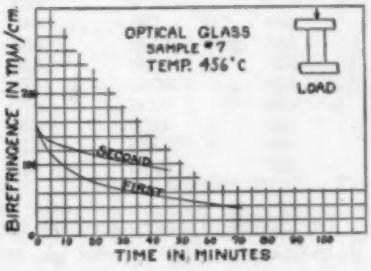


FIG. 13.

[11] Adams and Williamson also noted this initial rapid drop in the stress.

A careful examination of the data of Adams and Williamson discloses the same irregularity in the plotted curve. For example, the curve in Fig. 14 shows quite an abrupt change at 30 minutes and another at 150 minutes.

## VII. Comparison of the Equations and Their Effect upon Computations of the Annealing Time

The curve, Fig. 14, has been used to compare several of the equations. The dotted line shows the curve by the Adams and Williamson equation, the dot-dash line shows the same type of equation with $S$ squared, and the triangles show the points computed from the log formula which, in general, fits the data best.

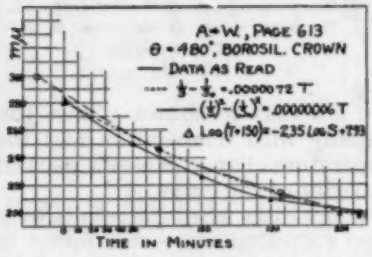



FIG. 14.

The accuracy of the representation by the log formula is interesting. Figure 10B shows the graph obtained by assuming values for $T$ which bring the first seven points of the data from Adams and Williamson (p. 622) into the best straight line. Using only these first seven points, the value of $A$ is found to be 1000 and the value of $m$, determined by measuring the slope, is $-4.04$.

Table III shows the values measured by Adams and Williamson, the corresponding time and the stress being read directly from the graph, Fig. 10B. It is evident that the calculated values fit the observations quite well.

TABLE III

| Observed value (A. and W.) (mμ) | Time (minutes) | Value read from graph (mμ) | Observed value (A. and W.) (mμ) | Time (minutes) | Value read from graph (mμ) |
|---|---|---|---|---|---|
| 672 | 0 | 668 | 400 | 7050 | 395 |
| 630 | 150 | 640 | 385 | 8370 | 380 |
| 555 | 1200 | 543 | 363 | 9825 | 367 |
| 520 | 1590 | 522 | 350 | 11310 | 355 |
| 478 | 2640 | 478 | 345 | 12780 | 345 |
| 470 | 3030 | 470 | 333 | 14550 | 337 |
| 445 | 4155 | 440 | 305 | 18720 | 317 |
| 428 | 5585 | 416 | 297 | 22780 | 300 |
| 420 | 5910 | 410 | 265 | 30360 | 280 |

Incidentally, there are now two equations which fairly well represent the data taken on this sample (A. and W., p. 622). They are as follows:

Fig. 6, $\log (T + 2000) = -3.182 \log S + 12.22$
Fig. 10B, $\log (T + 1000) = -4.04 \log S + 14.3$

The effect on the constants when $A$ is changed is thus apparent.

The great change in the time required for annealing to a small value of $S$, such as 22.5 mμ (3 mμ per centimeter) as determined by the log equation and that of Adams and Williamson is shown in Table IV. This table gives the comparative results obtained by the use of the log equations (reference

Nos. 1, 2, and 3 of Table I) and the equation of Adams and Williamson for a borosilicate crown glass at three different temperatures. These results indicate that at a temperature where the strain will relieve itself

TABLE IV

| No. 1 (p. 613) | | | | No. 2 (p. 613) | | | | No. 3 (p. 613) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | S | Computed S | | | S | Computed S | | | S | Computed S | |
| T | (observed) | A. and W. | B. and S. | T | (observed) | A. and W. | B. and S. | T | (observed) | A. and W. | B. and S. |
| 0 | 284 | 280 | 282 | 0 | 462 | 455 | 468 | 0 | 236 | 243 | 242 |
| 69 | 240 | 246 | 241 | 31 | 338 | 347 | 336 | 22 | 122 | 115 | 116 |
| 157 | 209 | 213 | 208 | 76 | 252 | 258 | 247 | 44 | 73 | 75 | 73 |
| 214 | 200 | 196 | 193 | 149 | 170 | 182 | 180 | 98 | 33 | 41 | 35 |
| | | | | 209 | 153 | 147 | 150 | 156 | 24 | 27 | 21.5 |
| | | | | 314 | 118 | 110 | 119 | | | | |
| 5,680 | | 22.5 | | 1927 | | 22.5 | | 150 | | | 22.5 |
| 77,120 | | | 22.5 | 4005 | | | 22.5 | 192 | | 22.5 | |

NOTE: The length of the optical path was 7.5 cm. Therefore the above values for $S$ should be divided by 7.5 to give mμ per cm.

quickly the formula of Adams and Williamson gives too long an annealing time, while at lower temperatures the annealing time by the Adams and Williamson equation is much too short.

## VIII. Observations on the Release of Strain

Starting with a slab of glass loaded as described in the early part of this paper, the black line seen across the loaded specimen is straight, showing that the strain is a maximum at the upper and lower surfaces and zero at the neutral axis. If the strain is released according to any formula in which its rate is other than the first power of $S$, the black line should gradually become $S$-shaped as in Fig. 15. In this figure it is assumed that the black line begins at a stress corresponding to 200 mμ at the surface. For the sake of simplicity, it is assumed that the rate of release is proportional to the square of $S$ and that the equation of Adams and Williamson is valid. Let the stress fall to 100 mμ at the top surface in time, $T$, equal to one unit. The computation of a series of points corresponding to various stresses along the stress line 200, after an elapsed time of $T$ equal to one unit, will enable the stress line corresponding to the end of this time interval to be plotted. This line is the heavy curved line (Fig. 15) below the numeral 100. The other lines, 67, 50, and 40, represent the strain at succeeding $T$ units. These can be rapidly obtained by projection as shown. All these lines are decidedly curved and follow directly from equation (3) or any of the log formulas which have been derived. Thus theory demands that the successive release curves must be curved.

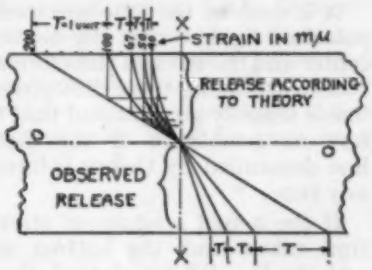



FIG. 15.

The amazing fact is, however, that these lines are all observed actually to be straight lines as shown below the neutral axis $OO$.

This divergency between the demands of theory and the observed result was further tested by means of a thick glass slab marked with lines on the surface so that strain observations could be taken at each surface and at measured distances in from the surface. Figure 16 shows the results of this experiment. The lines *B*, *C*, and *D* represent reference scratches on the face of the sample. Readings were taken on the bottom surface, along the lines *B*, *C*, and *D*, and the top surface, as rapidly as possible. It required from a minute to a minute and a half to make all of the readings so that the time along the top surface (bottom of picture) was actually about one minute later than is shown. It can be seen that a very slight divergence from the straight line developed along the lines *B* and *C*. If the observed points are projected on the corresponding straight lines and these points are connected with a straight line, the lines *XX* and *YY* result. The points along *D* fall upon the lines exactly.

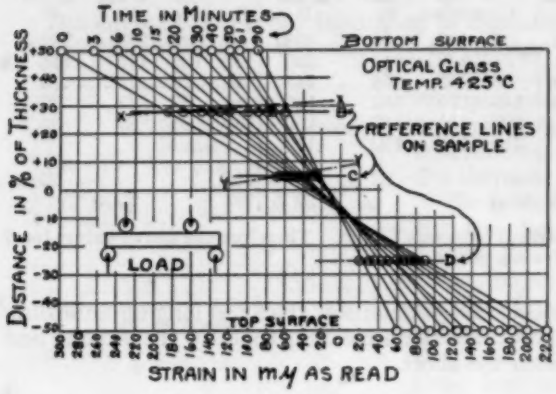



FIG. 16.

It is evident that the specimen was at a slight angle with the beam of polarized light so that the neutral axis did not appear to be at the exact center and the stresses therefore were slightly smaller along the top surface. Notwithstanding these difficulties, Fig. 16 proves definitely that the strain line is sensibly straight and that therefore no semblance of the *S*-shaped line demanded by theory is formed at any time.

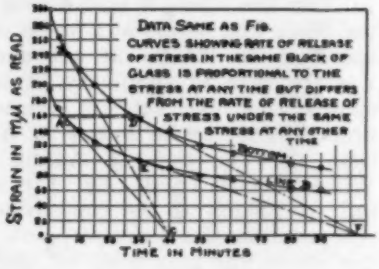

DATA SAME AS FIG.
CURVES SHOWING RATE OF RELEASE OF STRESS IN THE SAME BLOCK OF GLASS IS PROPORTIONAL TO THE STRESS AT ANY TIME BUT DIFFERS FROM THE RATE OF RELEASE OF STRESS UNDER THE SAME STRESS AT ANY OTHER TIME
STRAIN IN mμ AS READ
TIME IN MINUTES

FIG. 17.

If the actual readings of stress and time taken from the bottom surface and the line *BB* are plotted, there are obtained the two curves of Fig. 17. Tangents *BC* and *AC* (drawn at five minutes) intersect at *C*. Similarly tangents *DF* and *EF* (at thirty minutes) intersect at *F*. It is thus apparent that the rate of release of strain at any time is exactly proportional to the strain on each curve at that particular time. It is likewise apparent that the rates of release at *A* and *D*, which have the same stress but occur at different times, are entirely different in amount.

This observation leads to the conclusion that the rate of release of strain is directly proportional to the stress but the rate undergoes continual change as the time changes.

This change of rate with time has thus far been impossible to represent mathematically. For one thing, it may start at any time the observer wishes to take data so that the curves are not comparable in this respect.

## IX. Residual Birefringence

Many substances exhibit residual birefringence upon loading for some time and then removing the load. This phenomenon has already been referred to. Figure 18 shows the residual birefringence in a bar of synthetic resin. After a loading endwise in compression, the sample showed residual birefringence upon removal of the load amounting to 20% of the original load. This residual birefringence could be almost instantly removed by stretching the sample.

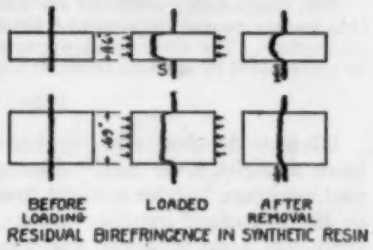



FIG. 18.

If the sample were left alone the birefringence gradually disappeared but it required about fourteen hours for the residual to disappear completely after a load had been applied for fifteen minutes. By mechanical means, namely, reversal of stresses, this strain could be removed in two or three minutes.

## X. Mechanical Acceleration of Annealing

It has been pointed out that the rate of release is very rapid during the first part of the annealing curve. Certain experiments have indicated that the reversal of stress causes release to take place at the high initial rate at each reversal even in glass. The residual strain, due to imperfect annealing in some glass samples, has been reduced almost to zero by two loadings and unloadings in about one quarter the time ordinarily required for annealing the same glass at the same temperature. Whether this system can be used commercially and whether all types of strain can be thus removed furnishes an interesting speculation which is now being investigated.

BAILEY & SHARP COMPANY, INCORPORATED
HAMBURG, NEW YORK

# COLOR CHANGES IN FLINT GLASS*

A. K. Lyle† and Donald E. Sharp‡

ABSTRACT

Decolorized glasses vary in their approach to neutral color depending upon their use and custom of manufacture. Iron, the chief coloring agent in colorless glass, produces several colors. The iron color is first controlled and then neutralized with its complementary color or colors furnished by a variety of oxides. The final tint may be neutral or not, depending upon the method of examination, and varies with changing conditions.

The decolorizing materials are subject to change after the glass is made. These changes are caused by heat and light radiations. Much research on color change is incomplete. The glass composition should be accurately known and the color should be represented by spectral transmissions.

## I. Introduction

Glass is decolorized to a degree depending upon its use. Milk bottles have a slight pink cast, tableware of fine quality may have a faint blue, and beverage bottles a slight green. These faint colors have become more or less standard for the various articles. Glass made from the usual ingredients, sand, soda ash, and lime, has a faint color due to the iron unavoidably introduced. This color due to iron is quite variable, depending upon the composition of the glass and the conditions of melting.

**(1) Colors Produced by Iron**

Herbert Jackson[1] described rather thoroughly the possible colors produced by iron and gave some indication of how they may be controlled. Glass may be colored by ferric oxide or ferroso-ferric oxide. No glasses have been observed in which metallic iron produces a color similar to gold ruby. Ferrous oxide produces a green. If zinc or magnesium is present the color is blue. Lithium also tends to produce blue from ferrous oxide.

**(2) Color Depends on Glass Compositions**

Ferric oxide by itself may range in color from reddish yellow, through brown, almost to black. The color produced in glass depends upon the composition of the glass. In three lead glasses of specific gravities 3.2, 3.8, and 4.8, each containing the same amount of ferric oxide, the color produced varies from no color in the glass with a specific gravity of 3.2 to a decided yellow in the 4.8 glass. Glasses containing considerable phosphate remain colorless when ferric oxide is introduced. If the glass is remelted under reducing conditions so as to reduce the iron, it becomes indigo blue. Ordinary sand-soda-lime glasses are difficult to color yellow with ferric oxide. Ferroso-ferric oxide gives neutral colors to glass. These results indicate the difficulties and possibilities of controlling the color produced by iron in glass.

**(3) Decolorizing**

To decolorize glass two steps may be taken. First, some effort may be made to control the color produced by the iron by control of melting conditions and by additional ingredients in the batch such as niter, antimony, arsenic, etc. The next step consists in matching the color from the iron by producing the complementary color or combination of colors so as to give the effect of no color in the glass.

* Presented at the Annual Meeting, American Ceramic Society, Pittsburgh, Pa., February, 1933 (Glass Division). Received March 31, 1933.

† Hazel-Atlas Glass Company, Washington, Pa.

‡ Bailey and Sharp, Inc., Hamburg, N. Y.

[1] *Nature*, **120**, 264 (1927).

The resulting glass will be clear but will have a lower light transmission and in some cases may appear gray. This neutralizing may be done with a number of materials and combinations, such as selenium, manganese, cobalt, nickel, and the rare earths.

The color produced by these so-called decolorizers varies with the condition of melting and with the glass composition. Selenium may produce a pink or yellow; manganese, green or purple; nickel, gray or purple; and cobalt, a royal blue or a purplish blue.

Since the original color due to iron is subject to variation and since the materials used for furnishing the complementary color are not consistent, it is not surprising to find variation in the final color.

## II. Temporary Changes

Before considering definite physical and chemical alterations, there are certain color changes which are physiological and which are important in preparing colorless glasses for definite purposes.

The thickness of glass has a great influence on its apparent color. Ordinary window glass viewed in the ordinary manner gives no sensation of color but, if viewed edgewise, exhibits a decided blue-green. This same effect to a lesser degree may be seen in glass plates. Often the edge appears to be a slight blue, and stacks of colorless plates will have a decided tint of blue or green. Smaller pieces made from the same glass may be colorless.

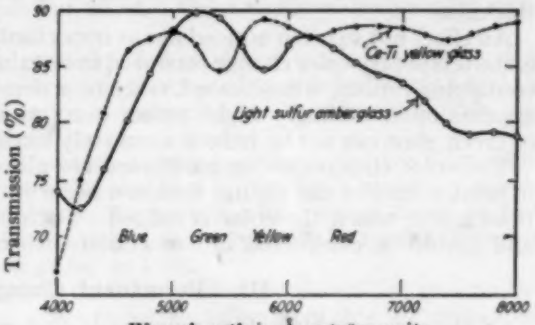



FIG. 1.

This effect of color change with thickness is due partly to a slight residual color in the glass after neutralizing and partly to the method of decolorizing which in most cases leaves regions of deep absorption in certain parts of the visible spectrum. Luckiesh states that a considerable thickness of glass may be useful in predicting the spectral transmission.

Moreover, the quality of the illumination in which a glass is viewed is an important consideration. For purposes of expert judgment as to the color quality of glass, it may be viewed with north light on a clear day. In actual practice this same glass may be used under artificial light from flame tint or yellow lamp globes or on a table cover made white by the addition of a slight blue tint. Under these conditions the glass may show a decided dark cast which was not apparent when it was viewed in daylight. In the case of some faintly colored glasses this change due to the quality of the illumination is quite marked. Topaz or yellow made with cerium and titanium oxides takes on a slightly red cast in artificial light. A light amber which nearly matches the topaz in daylight will become a dark glass with a slight green cast under artificial illumination.

A comparison of their spectral transmissions in the visible range shows

rather clearly the reason for this effect (Fig. 1). The cerium glass shows a deep absorption in the green and a rather sharp cut-off beyond the blue. The light sulfur amber has its highest transmission in the green with progressive absorption toward both the red and blue.

Very light cobalt blue which may be clear and brilliant in daylight becomes very dark and gray looking under artificial light. Glass colored with neodymium is blue in daylight but definitely pink in the light from an electric bulb. Since these same materials are used in smaller quantities as decolorizers, the effects may be the same but in a lesser degree in decolorized glass.

Glassware displayed under light of high intensity exhibits greater brilliancy. It is uncertain just how the term "brilliancy" can be expressed in scientifically exact terms. It is probably a function of the transparency and refractive index of the glass as well as the reflecting power of the surface. Polished glass surfaces appear brilliant because of their increased reflection. This phenomenon is used to advantage in glassware displays in which the display is illuminated with bare filament lamps that have a more intense light source than frosted lamps. The effect may be considered in a degree as complementary to the color-change effect produced by variation in thickness.

An effect not so often noticed nor as important for practical consideration is the temporary color change produced in certain glasses by heating. Glass containing cerium, when heated, takes on a decided golden color which disappears upon cooling. Light amber becomes more brown and the color of green glass can not be judged accurately until the material is quite cold.

The color changes so far mentioned are all of a temporary nature and in most examples the change does not occur in the glass but in the conditions under which the color is judged. Such changes are real to the eye and should be considered in connection with color changes in glass.

## III. Permanent Changes

Of the glasses which show permanent changes under the effect of heat or light, those containing manganese or selenium have been most often referred to and studied.

Glass decolorized with manganese often shows a slight pink. By passing this glass again through the leer, the color may be reduced to neutral. Selenium-containing glasses sometimes show a similar effect, but the color is more difficult to change. According to results presented by A. Cousen and W. E. S. Turner[2] only selenium-containing glasses which first showed a slight yellow tint indicating over-decolorization could be changed to a deeper color or pink by heating. This change took place at 1000 to 1300°F. The phenomenon was independent of the presence of arsenic or niter.

Small experimental melts, such as Cousen and Turner used, seldom give the same results as are obtained from larger commercial meltings. In glass from a tank furnace a decided pink cast has been developed in a number of cases by heating the object above the softening point and then cooling slowly to room temperature, even though the original glass was a definite green or "low" in color. The final color was dependent upon the rate of cooling near the softening point. Moreover, the color change could not be produced by reannealing. In general, larger pieces of glass will tend

[2] *Jour. Soc. Glass Tech.*, **9**, 111 (1925).

toward a pink or high color while smaller pieces from the same melting, which cool more rapidly, especially near the softening point of the glass, tend toward green or "low" color. This same effect has been produced by making two articles of the same external size and shape but with extra glass in one of them. The greater mass of glass cooled at a slower rate and was a faint pink color. The normal article subject to the same external conditions was a light green.

Many interesting and extensive studies have been conducted on the effect of ultra-violet radiation, X-rays, and radioactive rays on the color of glass. In these studies manganese plays the most spectacular rôle.

## IV. Observations Reported

No attempt is made to review the literature or to give a bibliography covering the work of the numerous investigations. It will be sufficient to state briefly the effect produced by the various rays.

Alpha rays produce only fluorescence but no permanent color change in glass. Beta rays probably cause some fluorescence and a change in color. The color is explained as due to the formation of colloidal particles in the glass from dissociated ions already present. The reaction is one of reduction. X-rays produce a similar effect. Color changes due to ultra-violet rays are caused by oxidation.

E. Rutherford[3] noted a reddish color produced in glass tubes by rays from radium emanation. The color penetrated to a definite depth and the colored glass had a higher index of refraction. The refractive index may have been higher in the beginning.

C. L. Ross[4] observed coloration in manganese glasses by ultra-violet radiation near 2900Å. The color was first brown, later becoming purple. If the glass were heated slightly, the purple color was produced at first. The color was destroyed by heating. This confirms the results of several previous investigators back as far as 1880.

Herbert Jackson[5] suggests that the color produced in manganese-containing glasses by ultra-violet radiation differs from that in glasses originally colored by manganese because the color produced by ultra-violet radiation may be destroyed by heating while glass originally colored is not changed. This is not strictly true since glass over-decolorized with manganese may generally be made neutral or lighter in tint by reheating.

C. W. Parmelee[6] reported the effect of X-rays on a number of compounds in fused borax beads. Chrome green became a brownish yellow color; a colorless gold ruby became very dark brown; a glass containing bismuth turned an orange yellow; and a colorless bead containing manganese became violet in tint. Most of the glass showed a slight darkening or gray cast after irradiation.

One of the writers has made a glass containing radium. The original glass was colorless, but after storage for nearly ten years developed a dark brown coloration. Heating the glass slightly (500°F) caused it to lose its color.

## V. Effect of Glass Composition

Much of the work on color is incomplete because of uncertainty concern-

[3] *Phil. Mag.*, **19**, 192 (1910).
[4] *Phys. Rev.*, **26**, 108 (1926).
[5] See footnote 1, p. 380.
[6] *Jour. Soc. Glass Tech.*, **13**, 279 (1929).

ing the composition of the glasses used. Chemical analysis alone does not tell the full story. It is not sufficient to know merely that the glass contains manganese or even how much manganese it contains. The melting conditions, the amount and condition of the iron which is always present, and the amount of such minor constituents as arsenic, niter, sulfate, and possibly the dissolved gases and water should be known.

In a number of investigations the materials have been described only as potash or soda glasses, and the resulting color attributed to this general classification without any regard for the small amount of iron or other impurities present. In this connection it has been noted that ultramarine is colorless if made from very pure materials, the conclusion being that iron is necessary for production of the desired blue color.

A third condition promoting color changes, which should not be considered as far different from the effects produced by light or short-wave radiation, is that due to chemical reactions during melting. Glasses melted with manganese in the presence of oxidizing agents show a purple color, while those melted under reducing conditions may be pale green. Selenium behaves in a similar manner except that it may color the glass amber under reducing conditions. The color produced by both selenium and manganese is affected by acid radicals. Sulfates tend to the production of a green color in glass so that additional decolorizer is needed. Just how much of the effect of the sulfate is on the state of oxidation of the iron and how much on the selenium or manganese is not known. The effect of lead and phosphates has already been mentioned. Potash and boron behave in a similar manner in affecting the color produced by various oxides.

To present accurate reports of color phenomena in glass the data should include spectral transmission curves as well as a description of the color or color change. This requirement is made evident by the possibility of the temporary color changes that have been mentioned. The eye synthesizes color and does not analyze it so that it is possible to produce the same color sensation in the eye by several combinations of spectral radiations.

In addition to the color data, the glass composition and melting conditions should be given. Particular mention should be made of the purity of materials and of the amount of iron unavoidably introduced.

# THE DETERMINATION BY X-RAY METHODS OF CRYSTALLINE COMPOUNDS CAUSING OPACITY IN ENAMELS*

By A. I. Andrews, G. L. Clark, and H. W. Alexander

ABSTRACT

The crystalline compounds present in vitreous enamels were determined by X-ray methods, particular reference being given to the opacifiers. It was shown that tin is present in enamels as crystalline tin oxide and antimony as the crystalline antimony pentoxide. Fluorspar added to the enamel contributes crystalline calcium fluoride. Cryolite and sodium silicofluoride contribute crystalline sodium fluoride. Other opacifiers and compounds such as zirconium oxide, zirconium silicate, calcium phosphate, arsenic oxide, and zinc sulfide added to enamels were studied. With the exception of the zirconium opacity the compounds causing opacity in enamels were identified alone and in the presence of other opacifiers.

## I. Introduction

The purpose of this investigation was to determine the crystalline compounds causing opacity in enamels when the various opacifiers were used, and to organize this information for future use in the study of enamels.

Although that property of white enamels called "opacity" has been studied from various angles by many investigators, there has been little work done to determine exactly the compounds causing the opacity. Many theories have been advanced, but little experimental proof has been given.

The crystalline compounds present were determined by X-ray examination of threads of the enamels, and the crystalline compounds present in the enamels were identified by comparison with standard patterns of known crystalline compounds.

For this problem, basic enamels of the dry-process cast-iron type were selected as being the best suited to the problem and the various opacifiers were added in combination with fluorspar and cryolite. During the investigation data regarding the smelting behavior of the enamel frits, the results of firing the enamel on test pieces, and the degree of opacity produced under the various conditions were also noted.

**(1) Review of the Literature** The literature upon this subject contains but little exact information or experimental data, although many theories concerning the cause or source of opacity in enamels and glasses are given by various writers and some few of the investigators have made X-ray determinations of opacifying compounds in glasses. Agde, Krause, and Lehmann[1] conclude that with the use of sodium fluoride (NaF) as the opacifying agent NaF separates from the cooling solvent and produces turbidity; when aluminum fluoride ($AlF_3$) is used NaF is formed; with calcium fluoride ($CaF_2$) the opacity is due to $CaF_2$ and NaF. Enequist[2] claims that the

* Received January 20, 1933.

See Progress Report on same subject in *Jour. Amer. Ceram. Soc.*, **14** [9], 634–39 (1931).

[1] (*a*) G. Agde and H. F. Krause, "Study of the Behavior of Fluoride Additions to Glasses and Enamels," *Z. angew. Chem.*, **40**, 525–33 (1927); *Chem. Abs.*, **21**, 2966 (1927); *Chem. & Ind.*, **46B**, 483 (1927); *Ceram. Abs.*, **6**, 374 (1927); Enamel Bibliography, p. 1.

(*b*) G. Agde, H. F. Krause, and W. M. Lehmann, "Behavior of Fluorides in Glasses and Enamels," *Z. angew. Chem.*, **40**, 804 (1927); *Chem. & Ind.*, **46B**, 654 (1927); Enamel Bibliography, p. 3.

(*c*) G. Agde and H. F. Krause, "Effect of Fluoride Additions to Glasses and Enamels. Causes of Fluorine Losses During Smelting of Glasses and Enamels with Fluoride Additions," *Z. angew. Chem.*, **40**, 886–95 (1927); *Chem. & Ind.*, **46B**, 702 (1927); *Chem. Abs.*, **21**, 3434 (1927); Enamel Bibliography, p. 1.

[2] E. Enequist, "Chemistry of Opaque Glass and Enamel," *Chem. Eng.*, **10**, 54 (1909); *Chem. Abs.*, **3**, 2865 (1909); Enamel Bibliography, p. 110.

opal color is due to silicon tetrafluoride ($SiF_4$). Zschimmer[3] states that the turbidity of opaque glass is the result of the precipitation of minute spheroids of fluorine compounds, principally NaF and $CaF_2$. Otremba[4] states that the opacity is due to crystals when cryolite is used and to fine air holes when fluorspar is employed. Bock[5] claims that fluorine has no influence whatever on the opacity of the resulting enamel. Ryde and Yates[6] state that the opacity of opal glasses has been attributed to alumina, aluminum fluoride, sodium silicofluoride, silica, silicon tetrafluoride, and aluminum silicates; however, their results show that the opacity of fluorine glasses is due either to NaF or $CaF_2$ or both. Other writers and investigators have stated that opacity was due to aluminum fluoride, silica, boric oxide, clay, oxides of tin, antimony, titanium, and zirconium (when compounds of these metals were used in the enamel) feldspar, colloidal silica, or alumina, and to occluded gases. Randall, Rooksby, and Cooper[7] found cristobalite crystallites present in glasses of vitreous silica, wollastonite, and sodium borate. These glasses, however, were transparent but are mentioned because similar lines were obtained on the X-ray patterns of some of the opaque enamel glasses.

The survey of the literature, however, reveals very little organized information regarding the cause of opacity in enamels used for iron and steel, and little or no work has been done to determine the opacifying compounds present in typical enamels when known opacifying agents are used.

## II. Selection of Enamels for Investigation

After experimentation on various compositions the basic enamel No. 49 was selected as being the best suited for additions of the various opacifiers to be studied. From this enamel, Nos. 48 and 50 were derived. The raw batch compositions are given below.

BASIC ENAMEL RAW BATCH COMPOSITIONS

| | No. 48 (%) | No. 49 (%) | No. 50 (%) |
|---|---|---|---|
| Feldspar | 32.1 | 32.1 | 32.1 |
| Borax | 24.7 | 24.7 | 24.7 |
| Soda ash | 3.7 | 3.7 | 3.7 |
| Soda niter | 2.9 | 2.9 | 2.9 |
| Whiting | 2.5 | 2.5 | 2.5 |
| Zinc oxide | 11.6 | 11.6 | 11.6 |
| Barium carbonate | 4.6 | 6.6 | 6.6 |
| Fluorspar | 4.0 | 6.0 | |
| Cryolite | 4.0 | | 6.0 |
| | 90.1 | 90.1 | 90.1 |

To these basic enamels 9.9% of one of the following opacifying agents was added: tin oxide, antimony oxide, sodium antimonate, zirconium oxide ("Opax"), titanium oxide, calcium phosphate (bone ash), zinc sulfide, aluminum fluoride, sodium fluoride, sodium silicofluoride, and arsenious oxide. The enamels were all leadless and of the dry-process cast-iron type.

Other miscellaneous enamels were tested. The R series[8] has been used

[3] E. Zschimmer, "Fluor-Opal and Theory of Opaque Glass Used in the Illuminating Industry," *Sprechsaal*, pp. 347–49, 364–66 (1930); *Chem. Abs.*, **24**, 3617 (1930).

[4] A. Otremba, "Fluorine in Enamel Melting," *Keram. Rund.*, **34**, 158–60 (1926); *Ceram. Abs.*, **5**, 299 (1926); *Chem. Abs.*, **20**, 3339 (1926); Enamel Bibliography, p. 231.

[5] B. Bock, "Importance of Fluorine in Enamels," *Chem.-Ztg.*, **32**, 730–32 (Aug. 1); *Chem. & Ind.*, **27**, 900 (1908); *Chem. Abs.*, **2**, 2718 (1908); Enamel Bibliography, p. 29.

[6] J. W. Ryde and D. E. Yates, "Opal Glasses," *Jour. Soc. Glass Tech.*, **10**, 274–94 (1926).

[7] J. T. Randall, H. P. Rooksby, and B. S. Cooper, "Structure of Glasses; Evidence of X-Ray Diffraction," *Jour. Soc. Glass Tech.*, **14**, 219–29 (1930).

[8] Taken from H. F. Staley, Bur. Stand. *Tech. Paper*, No. 142.

repeatedly for various cast-iron researches in the department. A, B, and D are simple enamel formulas of little value as good cast-iron enamels but suited for X-ray examination. Cryolite in the enamel is calculated both to $NaF_2 + Al_2O_3$ and as $NaF + AlF_3$. This was done because the normal procedure is to calculate the aluminum from the cryolite as $AlF_3$ but since no crystalline $AlF_3$ was found in any enamel by the X-ray examination it is probable that the aluminum was not present as $AlF_3$. It is therefore suggested that in enamel calculations based on oxide compositions all aluminum be figured as the oxide, $Al_2O_3$.

## III. Procedure

The raw frit batches were accurately weighed, screened through a 20-mesh sieve, and thoroughly mixed. When the gas-fired smelting pots had reached the desired temperature, approximately 2000°F, they were loaded with the raw batch. When the enamel was free from seeds, which was the indication that smelting was complete, threads of the enamel frit of about one-half millimeter diameter were drawn from the molten frit and were used as specimens for the X-ray examination. The X-ray specimens used to obtain the patterns of known crystalline compounds, which were compared with patterns of the crystalline compounds present in the fused enamel for identification, were made by drawing small glass tubes with an inside diameter of about one-half millimeter from Pyrex glass tubing and by filling the small tubes with the pure crystalline compound desired. The length of the tubes was about 2 inches. The powdered samples for the standard tubes were 200-mesh or finer in order that a sharp-line pattern might be obtained by the X-ray. Only an inch of material in the center of the tube was required to give a complete X-ray pattern.

The test specimens were placed in position on a quadrant cassette and set on a General Electric multiple diffraction apparatus. This method of X-ray examination is the Hull-Debye-Scherrer powder method[9] and was selected as it gave the easiest and most accurate determination for work of this kind. The time of exposure of the different samples to the X-ray varied over a wide range. No attempt was made to keep this factor uniform as only identification of the crystalline compounds was desired.

After sufficient threads had been drawn the remainder of the molten frit was quenched in water, dried, and ground to 100-mesh; then the regular cast-iron test pieces were enameled and the firing properties and degree of opacity were noted. Some X-ray work was done on specimens of sheet steel and cast iron enameled with the test enamels.

Attempts were made using the monochromatic pinhole method, but this work was not carried far since a greater amount of sample could be exposed to the X-rays and comparison was easier and more accurate by the first method. In the case of enamels containing zirconium oxide ($ZrO_2$), however, it was necessary to remove the zirconium-oxide filter in the quadrant cassette to obtain a satisfactory pattern.

A discussion of the theory of X-rays would be out of place and too lengthy for this paper and therefore the reader is referred for this information to the footnote references.

[9] (*a*) G. L. Clark, X-Ray Metallography of 1929; (*b*) *ibid.*, Applied X-Rays; (*c*) Terrill and Ulrey, X-Ray Technology; (*d*) W. H. Bragg, Introduction to Crystal Analysis; (*e*) W. H. Bragg and W. L. Bragg, X-Ray and Crystal Structure; (*f*) W. W. Pullin, "X-Ray Crystal Analysis," *Engineer*, July 4, 1930.

It is sufficient to state that all crystalline substances belong to a definite crystallographic system having a definite size and shape of unit crystal. X-rays are diffracted by crystalline compounds and if a photographic plate or film is so placed that the compound is between the plate or film and the X-ray source, a pattern which is characteristic of the compound is obtained on the plate or film. These patterns can be measured and, with the proper calculations, the size or system of the unit crystal can be obtained and thus identified, or the patterns can be compared with standard patterns of known pure compounds for identification.

## IV. Discussion

**(1) Smelting** During the smelting of the raw batches it was noted that the different opacifiers had a decided effect on the fusibility of the enamel frit. In the enamels containing the tin oxide and antimony oxide, seeds were difficult to eliminate. The sodium antimonate and zirconium oxide enamels fused well, while the high fluoride enamels were easily and quickly fused. In the zinc sulfide, bone ash or calcium phosphate, arsenious oxide, and titanium oxide enamels, the opacifiers did not disperse uniformly into the glass but remained as flakes throughout the mass. In the sodium fluoride, aluminum fluoride, and sodium silicofluoride enamels, the opacifiers completely dissolved in the enamel glass and then recrystallized on cooling to give opacity to the enamels. This is also true of the special enamels, A, B, and D.[10]

**(2) Firing** The high fluoride enamels matured at a lower temperature and in shorter time than the enamels with less fluorine.

**(3) Opacity** Tin oxide, antimony oxide, sodium antimonate, and zirconium oxide gave the best opacity, as would be expected.

**(4) Firing Conduct** All enamels tested had good glossy surfaces but many had a few small pinholes which probably could be eliminated by adjusting firing conditions and application. The high sodium enamels, those containing sodium fluoride and sodium silicofluoride as the opacifiers, crazed because of the great difference in expansion between the enamel and the iron.

**(5) Relation of X-ray Exposure to Crystalline Compounds Present** The principal opacifying compounds gave good patterns with any period of exposure over 48 hours for enamels containing tin oxide, antimony oxide, and sodium antimonate in which there was little solution or volatilization of the opacifier. The other enamels required longer exposure due probably to volatilization or solution of the opacifier, thus lowering the percentage of crystalline material in the glass. No attempt was made to determine the exact time of exposure necessary. The 48 series of enamels has a possible maximum crystalline content of 15.9%, the 49 series 17.5%, and the 50 series 13.5%. Actually these percentages were much lower due to volatilization of fluorine and solution in the enamel glass and it is probable that not over 10% was present in most cases. This fact alone shows the necessity for long exposure.

**(6) Discussion of Results** (1) It was noted from the relative heaviness of the lines on the X-ray patterns of the 48 series that when both $CaF_2$ and NaF were present, the $CaF_2$ lines

[10] See paragraph (17), (18), and (19), p. 390.

were heavier. This is, no doubt, due to the presence of 4% fluorspar and only 4% cryolite which, however, contains but 2.4% NaF. Nevertheless, $CaF_2$ is more active in giving opacity itself than NaF but the quality of the cryolite enamels excels that of the $CaF_2$ enamels. As $CaF_2$ and NaF, however, are soluble in the glass and recrystallize on cooling, the rate of cooling is a deciding factor on the amount of crystalline $CaF_2$ and NaF present in the finished enamel.

(2) The opacity in the zinc sulfide, calcium phosphate, arsenic oxide, and titania enamels increased greatly on reheating, by comparison with their thread tests from smelting which showed little or no opacity, the enameled iron showing good opacity in most cases. The threads drawn from reheated molten enamel were used for the X-ray examination.

(3) The X-ray pattern for tin oxide enamels containing fluorspar showed the presence of crystalline calcium fluoride, but when the tin oxide was replaced by antimony oxide, sodium antimonate, zinc sulfide, or calcium phosphate, no calcium fluoride crystals were present.

(4) In the zirconium oxide enamels containing fluorspar in the raw batch, $CaF_2$ is the principal opacifying compound with the unidentified compound (thought to be one containing zirconium) present in lesser amounts. This compound is not "Opax," pure zirconium oxide ($ZrO_2$), or zirconium silicate ($ZrSiO_4$).

(5) Antimony trioxide ($Sb_2O_3$) is oxidized in the smelting to antimony pentoxide ($Sb_2O_5$).

(6) Sodium antimonate is decomposed during smelting to $Sb_2O_5$ which is the crystalline compound causing opacity and to sodium oxide ($Na_2O$) which goes to form part of the glass.

(7) In enamels containing aluminum fluoride or sodium silicofluoride in the raw batches, neither $AlF_3$ nor $Na_2SiF_6$ remain as crystalline compounds. The crystalline compounds $CaF_2$ and NaF from the fluorspar and cryolite, respectively, present in the basic enamels are the opacifying compounds.

(8) In the zinc sulfide (ZnS) enamels the crystalline ZnS is the principal opacifying compound with an unidentified compound present in smaller amounts.

(9) Several enamels, *e.g.*, 50CP, 48ZnS, 48Ti, and others, gave patterns on X-ray examination showing the presence of crystallites of extremely small size, indicated by the broad band on the X-ray pattern. This is probably a form of silica and is in accord with the work of Randall, Rooksby, and Cooper.[7]

(10) The unidentified crystalline compound in the $TiO_2$ enamels is not the compound $TiO_2$ itself. Also, in the $As_2O_3$ enamels it is not the compound $As_2O_3$. Whether or not it is $As_2O_5$ has not been definitely established.

## V. Examination of Enamels for Presence of Crystalline Compounds by X-rays

(1) Enamel 48Sn (tin oxide, fluorspar, and cryolite) showed crystalline $SnO_2$ as the principal opacifying compound with $CaF_2$ and NaF in lesser amounts.

(2) Enamels 49Sn (tin oxide and fluorspar) and 50Sn (tin oxide and cryolite) showed only crystalline $SnO_2$.

(3) Enamels 48Sb (antimony oxide, fluorspar, and cryolite), 49Sb (antimony oxide and fluorspar), 50Sb (antimony oxide and cryolite), 48NA (sodium antimonate, fluorspar, and cryolite), 49NA (sodium antimonate and fluorspar), and 50NA (sodium antimonate and cryolite) in the raw batch showed only crystalline $Sb_2O_3$ as the opacifying compound.

(4) Enamels 48Zr (zirconium oxide, fluorspar, and cryolite) and 49Zr (zirconium oxide and fluorspar) showed crystalline $CaF_2$ to be the principal opacifying compound in the fused enamel and also some other crystalline compound which is thought to be a zirconium compound.

(5) Enamel 50Zr (zirconium oxide and cryolite) showed crystalline NaF to be the principal opacifying compound in the fused enamel and also some other crystalline compound which is thought to be a zirconium compound.

(6) Enamels 48NaF (sodium fluoride, fluorspar, and cryolite) and 49NaF (sodium fluoride and fluorspar) showed both crystalline $CaF_2$ and NaF as the opacifying compounds.

(7) Enamel 50NaF (sodium fluoride and cryolite) showed only crystalline NaF as the opacifying compound.

(8) Enamels 48$AlF_3$ (aluminum fluoride, fluorspar, and cryolite) and 49$AlF_3$ (aluminum fluoride and fluorspar) showed only crystalline $CaF_2$ as the opacifying compound.

(9) Enamel 50$AlF_3$ (aluminum fluoride and cryolite) showed only crystalline NaF as the opacifying compound.

(10) Enamel 48NSF (sodium silicofluoride, fluorspar, and cryolite) showed crystalline $CaF_2$ to be the principal opacifying compound with some NaF present.

(11) Enamel 49NSF (sodium silicofluoride and fluorspar) showed only crystalline $CaF_2$ as the opacifying compound in the fused enamel.

(12) Enamel 50NSF (sodium silicofluoride and cryolite) showed only crystalline NaF as the opacifying compound.

(13) Enamels 48ZnS (zinc sulfide, fluorspar, and cryolite), 49ZnS (zinc sulfide and fluorspar), and 50ZnS (zinc sulfide and cryolite) showed crystalline ZnS as the principal opacifying compound in the fused enamel with another compound present but as yet unidentified.

(14) Enamels 48CP (calcium phosphate, fluorspar, and cryolite), 49CP (calcium phosphate and fluorspar), and 50CP (calcium phosphate and cryolite) showed only crystalline $Ca_3(PO_4)_2$ as the opacifying compound.

(15) Enamels 48$As_2O_3$ (arsenious oxide, fluorspar, and cryolite), 49$As_2O_3$ (arsenious oxide and fluorspar), and 50$As_2O_3$ (arsenious oxide and cryolite) showed a crystalline compound to be present in the fused enamel, which as yet has not been identified.

(16) Enamels 48Ti (titanium oxide, fluorspar, and cryolite), 49Ti (titanium oxide and fluorspar), and 50Ti (titanium oxide and cryolite) showed a crystalline compound not yet identified.

(17) Enamel A (fluorspar) showed only crystalline $CaF_2$ as the opacifying compound.

(18) Enamel B (cryolite) showed only crystalline NaF as the opacifying compound.

(19) Enamel D (fluorspar and cryolite) showed both crystalline $CaF_2$ and NaF as the opacifying compounds.

(20) Enamel R42 (tin oxide and cryolite) showed only crystalline $SnO_2$ as the opacifying compound.

(21) Enamel R46 (tin oxide, fluorspar, and cryolite in the raw batch) (a lead enamel) showed crystalline $SnO_2$ and $CaF_2$ with some NaF as the opacifying compounds in the fused enamel.

(22) Enamels R49 (sodium antimonate and fluorspar) (a lead enamel), R52 (antimony oxide, fluorspar, and cryolite), and N6 (sodium antimonate, sodium silicofluoride, and titanium oxide) (a lead enamel) showed only crystalline $Sb_2O_5$ as the opacifying compound.

## VI. General Summary

(1) All enamels tested showed the presence of crystalline compounds indicating that the opacity of enamels was due in part or wholly to these crystalline compounds.

(2) The X-ray proved to be the only means of identifying these crystalline compounds as they were too small in size to be determined with the microscope.

(3) Tin oxide, when used as the principal opacifying agent, remained as crystalline $SnO_2$ giving opacity to the enamel. The tin oxide that caused the opacity was not dissolved by the smelting. Fluorspar, when used with tin oxide, was present as crystalline $CaF_2$ in smaller quantities. Cryolite, when used with tin oxide, remained soluble in the enamel glass and crystalline NaF did not crystallize to an extent which gave a pattern on the X-ray examination. When cryolite was used with fluorspar and tin oxide, crystalline NaF as well as $CaF_2$ were present in the fused enamel.

(4) Crystalline $Sb_2O_5$, antimony pentoxide, was the crystalline compound causing opacity in enamels containing commercial antimony oxide or sodium antimonate. The commercial antimony oxide was oxidized during smelting to the antimony pentoxide, $Sb_2O_5$. It is assumed that sodium antimonate reacts with the enamel to form antimony pentoxide, $Sb_2O_5$, and the $Na_2O$ goes to form part of the glass.

(5) The crystalline compounds causing the opacity in enamels containing zirconium oxide, $ZrO_2$, or "Opax," as the principal opacifier with fluorspar or with cryolite as the secondary opacifier were crystalline $CaF_2$ in the enamel containing fluorspar and NaF in the cryolite enamel with an unidentified compound, which was not "Opax," pure $ZrO_2$, or $ZrSiO_4$, also present in smaller amounts. It may have been some other form of the oxide or possibly a fluoride of zirconium. Zirconium enamels seemed to retain a greater per cent of their fluorine content than enamels containing the other opacifiers.

(6) Sodium silicofluoride, fluorspar, cryolite, aluminum fluoride, or sodium fluoride gave opaque glass when used as opacifying agents alone. Sodium silicofluoride when used as the principal opacifying compound with fluorspar as the secondary opacifier gave an opaque enamel containing only crystalline $CaF_2$, while with cryolite as the secondary opacifier the enamel contained only crystalline NaF. When fluorspar was used alone the enamel contained only crystalline $CaF_2$. When cryolite was used alone the enamel contained only crystalline NaF, the remainder of the cryolite being retained in the glass. With aluminum fluoride the opacity was due to crystalline $CaF_2$ when fluorspar was the secondary opacifier and to NaF when cryolite was the secondary opacifier. No crystalline $AlF_3$

was found in any of the enamels tested. When sodium fluoride was used as the principal opacifier with fluorspar as the secondary opacifier both crystalline NaF and $CaF_2$ were present, while with cryolite as the secondary opacifier only crystalline NaF was present. In all enamels in which the opacity was due to either crystalline $CaF_2$, NaF, or to both, the crystalline compounds were soluble in the enamel glass and then recrystallized on cooling, the degree of opacity depending upon the rate of cooling.

(7) Sodium silicofluoride, fluorspar, and cryolite aided in the development of opacity when used with tin oxide, antimony oxide, or sodium antimonate but did not in themselves in the presence of these metal oxides cause opacity, with the exception of fluorspar and cryolite with tin oxide.

(8) The identification of $Ca_3(PO_4)_2$ crystalline calcium phosphate in the fused enamel was unexpected and, although the patterns obtained seemed conclusive, more work should be done on this type of enamel before final conclusions are drawn.

(9) The development of satisfactory dry-process cast-iron enamels with good opacity by the use of zirconium oxide, $ZrO_2$ ("Opax"), and zinc sulfide, ZnS, in the same percentages as in the tin oxide, antimony oxide, and sodium antimonate enamels may be of commercial value and is worthy of fuller study and research.

(10) The identification of the unknown compounds should be made so as to complete more fully the information regarding the opacity caused by crystalline compounds.

# THE ACTION OF WASTE-WOOD ASH ON REFRACTORIES*

By Kenneth G. Skinner and Norman L. Field

ABSTRACT

A description is given of several industrial waste-wood furnaces with auxiliary oil-firing equipment to show the types of installations and the slagged areas. In the tests, wood ash from industrial furnaces was blown onto panels of various refractories which had been heated in an oil flame. Chemical analyses and properties of the brick tested, the waste-wood ash, the slags from industrial furnaces, and the test furnace are given. All of the refractories suffered in this high lime-alkali slag, but silicon carbide gave the best resistance. The tests indicated that the absorption of the fireclay and diaspore types of brick was more important in their resistance than the alumina-silica ratio. Petrographic studies of the slag-brick interface showed the presence of mullite in all of the fireclay, kaolin, and diaspore brick.

## I. Introduction

The purpose of this investigation was to determine the action of waste-wood ash on refractories when oil-firing was used as an auxiliary source of heat. Waste wood has been used extensively in the Pacific northwest for a great many years with little trouble with slagging until the last few years when oil was introduced as an auxiliary fuel.

## II. Description of Furnaces and Slagged Areas

**(1) Types of Furnaces** A number of the boiler installations studied were originally designed for waste-wood firing, while others had been converted from other types. The oil-firing apparatus may or may not have been included in the original installation. Figures 1 and 2 show furnaces designed for waste wood, and Fig. 3 for waste wood and oil.

In all cases the waste wood is burned in a Dutch-oven type of fire box, producing gases which are burned in a large combustion chamber. Furnaces that have not been properly designed with sufficient combustion space for the gases from both the waste wood and the oil give not only poor combustion but also severe slagging from the associated reducing conditions and "hot spots." The worst slagging occurs in the "hot spots" along the fuel and ash border lines because it is here that the fluxes are usually concentrated and higher temperatures are reached. Figures 1, 2, and 3 show the areas of slagging in the general types of furnaces. Spalling generally occurs in the opening between the Dutch oven and the larger combustion chamber, especially if the opening is restricted as shown in Fig. 2.

## III. Character of the Fuels

**(1) Waste Wood** The wood available for fuel can be considered under three general classifications according to water content as follows:

(*a*) Sawdust and slabs contain from 30 to 50% moisture when the logs are transported to the mill dry, and as high as 70% when water-transported. The bark and shavings from pulp wood may contain over 70%. The

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average waste wood, as used in the industrial plants, has an average water content of 50%.

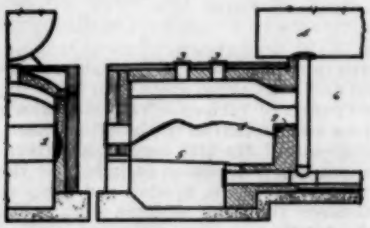

FIG. 1.—Waste-wood furnace: (1) slag line, (2) spall line, (3) waste-wood fuel feed, (4) boiler, (5) grate, and (6) combustion chamber.

(*b*) Refuse from planing mills and finished lumber operations using air-dried lumber has an average moisture content between 15 and 25%.

(*c*) Refuse from manufacturing establishments using kiln-dried lumber has an average moisture content between 5 and 7%.

The theoretical flame temperature of wood with a moisture content of 50% ranges from 3000°F with no excess air to 1950° with 100% excess air. In the plant of the Grays Harbor Railway and Light Company the average flame temperature was found to be 2325°F (1273.9°C). Table I gives the analyses and calorific value of dry wood.

The hogged fuel of Table I was composed of 75% Douglas fir and 25% unclassified material. The proximate analysis was volatile matter 81.5, fixed carbon 18.0, and ash 0.5%.

Waste-wood fuels containing hemlock have a high content of tannic and acetic acids.

**(2) Fuel Oil** Various grades of oil are used for fuels, the most common being the so-called fuel oil. The analyses of some oils are given in Table II.

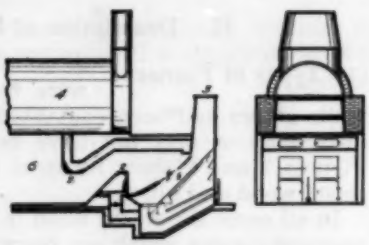

FIG. 2.—Waste-wood furnace: (1) slag line, (2) spall line, (3) waste-wood fuel feed, (4) boiler, (5) grate, and (6) combustion chamber.

**(3) Analyses of Ash from the Two Fuels** From the analyses in Tables I and II, it can be seen that although the per cent of ash is low, the accumulation of ash obtained over a period of time would cause trouble as the ash contains chemically active ingredients

TABLE I

ULTIMATE ANALYSES AND CALORIFIC VALUES OF DRY WOOD[a]

| Kind of wood | C | H | O | N | Ash | B.t.u./lb. |
|---|---|---|---|---|---|---|
| Oak | 50.16 | 6.02 | 43.36 | 0.09 | 0.37 | 8316 |
| Ash | 49.18 | 6.27 | 43.91 | 0.07 | 0.57 | 8480 |
| Elm | 48.99 | 6.20 | 44.25 | 0.06 | 0.50 | 8510 |
| Beech | 49.06 | 6.11 | 44.17 | 0.09 | 0.57 | 8591 |
| Birch | 48.88 | 6.06 | 44.67 | 0.10 | 0.29 | 8586 |
| Fir | 50.36 | 5.92 | 43.39 | 0.05 | 0.28 | 9063 |
| Pine | 50.31 | 6.20 | 43.08 | 0.04 | 0.37 | 9153 |
| Average | 49.56 | 6.11 | 43.83 | 0.07 | 0.42 | 8671 |
| Hogged fuel[b] | 50.00 | 6.00 | 43.10 | 0.40 | 0.50 | |

[a] A. Gottlieb, "Elementary Composition of Wood," *Jour. prakt. Chem.*, **28** [2], 385 (1883).

[b] H. Hirsch, "Fuel and Refractory Lining Material," *Chem. Abs.*, **18**, 2588 (1924).

which would attack the refractories. Table III gives the analyses of ashes from these two fuels.

Ash No. 1 was from a Pacific northwest hogged fuel consisting of hemlock and fir, No. 2 from waste wood, No. 3, the sooty residue in a boiler using California fuel oil, and No. 4 from a mid-continent petroleum coke. The hogged fuel and the waste-wood ashes contained hard particles and lumpy masses, while the oil residue was a soft, sooty, pulverulent, carbonaceous material. In one installation the wood ash was finely divided but like the other wood ash it contained hard particles. Abrasive action of the hard ash may affect the degree of slagging.

FIG. 3.—800 H.P. Ladd boiler, waste wood and oil fired: (1) fuel regulating gate, (2) height of division wall, (3) oil burners, (4) tuyères, (5) forced air dampers in walls, and (6) air-tight ash doors.

## IV. Method of Feeding Fuels

The waste-wood fuel is fed from the top and allowed to accumulate on the grate. The method used at the power plant of the Grays Harbor Railway and Light Company in Aberdeen, Washington, is typical of the larger installations and will be described in detail.

**(1) Waste Wood** The hogged fuel is fed through two rectangular openings in the arch of a gas-producer chamber, and piles up in two cone-shaped masses 6 feet 6 inches high at the center and

TABLE II

PROPERTIES OF FUEL OIL[a]

| Physical properties | No. 1 | No. 2 | No. 3 | No. 4[b] |
|---|---|---|---|---|
| Specific gravity at 60° | 0.958 | 0.961 | | |
| Viscosity, Saybolt-Furel at 122° (sec.) | 125 | 160 | | |
| Flash point, Pensky-Martens (degrees) | 288 | 212 | | |
| Sediment (%) | 0.04 | 0.03 | | |
| **Chemical analysis** | | | | |
| Carbon | 85.00 | 85.30 | 83.70 | 86.70 |
| Hydrogen | 11.40 | 11.50 | 13.00 | 6.00 |
| Oxygen | | | 1.30 | 3.00 |
| Nitrogen | 0.20 | 0.20 | 2.00 | 0.10 |
| Sulfur | 1.90 | 1.80 | 1.30 | 3.00 |
| Ash | 0.06 | 0.07 | | 0.10 |
| Moisture | 3.10 | 0.00 | | 3.30 |
| Calorific value (B.t.u./lb.) | 18,540 | 18,690 | | |

[a] Ralph A. Sherman, "A Study of Refractories Service Conditions in Boiler Settings," U. S. Bur. Mines *Bull.*, No. 334 (1931).
[b] Coal-tar oil.

2 feet at the sides. There are two gas chambers for the hogged fuel, each 8 feet square and 10 feet high, separated by a 9-inch brick wall. Back of these two chambers is the combustion chamber 17 feet long by 10 feet wide by 20 feet high to the tubes. The combustion chamber is coated with

1/4 inch of plastic refractory material. The floor consists of 9 inches of fire brick, 14 inches of diatomaceous earth, and 12 inches of ordinary brick. An 18-inch air duct is under the floor (see Fig. 4).

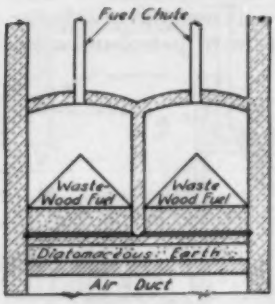


FIG. 4.—Waste-wood furnace of the Grays Harbor Railway & Light Co. Vertical cross-section at the bag wall.

The flames from the hogged fuel sweep down from the Dutch oven and then up toward the tubes in a path like the letter "J." The draft carries unburned fuel and ash over into the combustion chamber and deposits it in an elliptical cone 3 feet high. After three months' operation about 10 inches of ash collects on the floor of the combustion chamber.

**(2) Fuel Oil** The burners are of the high oil-pressure and low air-pressure type. Secondary air is admitted at the burner ports which are circular openings in the back of the combustion chamber 12 inches in diameter and lined with refractory material. There are 12 burners arranged in 2 banks on 30-inch centers, and so designed that they may operate at their greatest capacity in two minutes. Figure 5, a side section of the furnace, shows the location of the principal parts and the general paths of the waste-wood and oil flames.

TABLE III

ANALYSES OF WASTE-WOOD AND FUEL-OIL ASHES

| | No. 1 | No. 2 | No. 3 | No. 4[a] |
|---|---|---|---|---|
| Moisture | | | 10.66 | |
| Volatile | | 17.61 | 19.61 | |
| Phosphorus pentoxide | | | 15.90 | |
| Carbon dioxide | | 20.10 | | |
| Sulfur trioxide | | | 7.12 | 1.15 |
| Silica | 21.4 | 13.19 | 11.44 | 43.99 |
| Alumina | 5.6 | 3.44 | 16.74 | 1.26 |
| Ferric oxide | 7.7 | 4.74 | 9.67 | 27.71 |
| Calcium oxide | 45.5 | 27.96 | 0.91 | 22.45 |
| Magnesium oxide | 1.3 | 0.82 | 0.59 | |
| $Na_2O$ and $K_2O$ | | 11.26 | 7.32 | |
| $Na_2O$ | 6.4 | | | |
| $K_2O$ | 12.0 | | | |
| NaCl | | | | 3.32 |
| Total | 99.9 | 99.12 | 99.96 | 99.88 |

[a] L. Litinsky, "Refractories for Boilers," *Ceram. Abs.*, **4**, 105 (1925).

**(3) Character of the Slags** Most of the slags were hard dark green to black silicates, with a subconchoidal fracture, like obsidian but with a greater specific gravity. The slag from the combustion chamber of the Aberdeen plant, however, was gray and brittle and did not have the glassy appearance of the other slags. Chemical analyses were made of the different commercial and laboratory slags and tabulated in Table IV. The slag accumulated in the Dutch oven on the

floors of the combustion chambers after running off the walls and around the oil burner ports.

**(4) Description of Slag Samples** Slags Nos. 1, 2, and 3 are from the boilers of Crown Willamette Paper Company, Camas, Wash.; Slag No. 4 is hogged-fuel slag from the boilers of Washington Pulp and Paper Company, Port Angeles, Wash.; Slag No. 5 is from the wood-fired drier of Builder's Brick Company, Seattle, Wash.; Slags

TABLE IV

SLAG ANALYSES

| Slag No. | $SO_3$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $Na_2O$ and $K_2O$ | $VdO$ | $NiO_2$ | $TiO_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 42.42 | 24.86 | 7.14 | 27.50 | 0.60 | 7.63 | | | |
| 2 | | 44.75 | 26.00 | 7.85 | 15.50 | 0.62 | 5.00 | | | |
| 3 | | 46.75 | 23.73 | 7.33 | 15.50 | 0.72 | 6.04 | | | |
| 4 | | 25.12 | 4.70 | 27.36 | 26.02 | 7.61 | 9.10 | | | |
| 5 | | 54.10 | 22.15 | 1.99 | 6.53 | Trace | 15.30 | | | |
| 6 | | 43.42 | 10.58 | 22.06 | 18.14 | 2.03 | 9.10 | | | |
| 7 | | 28.93 | 17.82 | 28.71 | 16.64 | Trace | 8.18 | | | |
| 8 | | 36.31 | 9.46 | 24.28 | 19.45 | 1.02 | 8.68 | | | |
| 9 | 0.1 | 53.4 | 26.4 | 4.4 | 1.99 | 0.9 | 7.5 | 2.0 | 0.4 | |
| 10 | 40.3 | 5.7 | 1.4 | 5.1 | 4.7 | 1.2 | 25.7 | 12.3 | 2.8 | |
| 11 | 29.1 | 7.4 | 4.33 | 6.7 | 7.6 | 1.9 | 21.9 | 18.3 | 2.8 | |
| 12 | | 49.00 | 25.90 | 8.00 | 0.90 | 1.20 | 4.20 | 6.10 | | 0.97 |

Nos. 6, 7, and 8 are waste-wood and oil-fuel slags from boilers of the Grays Harbor Railway and Light Company, Aberdeen, Wash.; Slag No. 9 is from the bottom of an oil-fired furnace[1]; Slag No. 10 is dust from the boiler tubes of an oil-fired furnace[1]; Slag No. 11 is ash of coke residue from an oil-fired furnace[1]; and Slag No. 12 is Pamico oil-fired furnace slag.[2]

## V. Tests

**(1) Simulative Service Slag Test** A rectangular furnace was used having an inside width of 18 inches, a height of 29 inches, and a length from the burner doorway to the bag wall of 40 inches. An oil flame played horizontally onto the center of a twelve test-brick panel built against the bag wall and inclined about 20° from the vertical. The $2^1/_2$- by 9-inch faces were exposed to the action of the flame and the slag. The brick were separated from each other by thick fireclay joints to facilitate removal after the test. Two brick of each brand were placed in different parts of the panel. Figure 6 shows the arrangement of the furnace and the spraying apparatus.

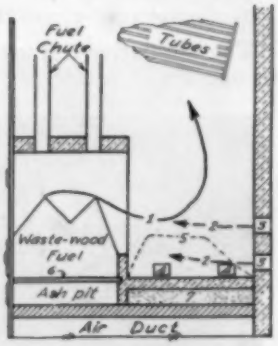


FIG. 5.—Same furnace as shown in Fig. 4; side section.

**(2) Heating and Spraying** The furnace was heated at an average rate of 850°F per hour to 2000°F and at about

[1] See footnote (*a*), Table I, p. 394.
[2] See footnote (*a*), Table II, p. 395.

100°F per hour to about 2800°F, after which the temperature was held as constant as possible until the end of the test. A Leeds and Northrup optical pyrometer was used for the panel-temperature measurements.

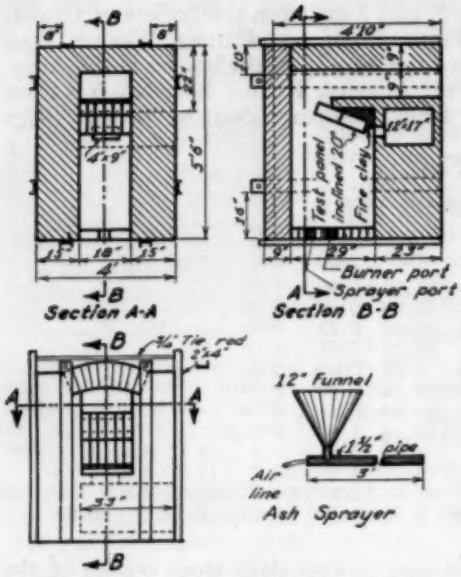


FIG. 6.—Test furnace and ash sprayer.

The ash was dried, screened through a 4-mesh sieve, and blown onto the panel at 15-minute intervals through a hole in the doorway above the burner. The spraying apparatus consisted of a 12-inch funnel connected to a compressed air injector. Photographs were taken of the test panels before and after the tests to show the relative action on each brick. Figures 7 and 8 show slagged brick in comparison with unslagged brick. The absorption of the brick was determined by boiling for one hour, and the volumes of the brick were found in an overflow volumeter after soaking. This method was used because the volumes of the irregularly shaped slagged brick could be found in the same manner.

## VI. Advantages of Test

The simulative test used had the following advantages: (1) it was simple to operate at either high or low temperatures; (2) it simulated service

FIG. 7.—Sections of slagged brick compared with unslagged brick. Left to right: kaolin 1, fire clay 2, fire clay 6, fire clay 5, high aluminous, and diaspore 1.

TABLE V
CHEMICAL ANALYSES OF THE BRICK TESTED

| Brick | | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ and $Na_2O$ | $TiO_2$ | $Cr_2O_3$ | Total |
|---|---|---|---|---|---|---|---|---|---|---|
| Fire clay | 1 | 56.99 | 38.39 | 3.99 | 1.01 | 0.65 | | | | 100.63 |
| | 2 | 45.50 | 51.90 | 1.44 | 1.64 | Trace | | | | 100.48 |
| | 3 | 66.92 | 29.17 | 2.95 | 0.82 | Trace | 0.14 | | | 100.00 |
| | 4 | 62.68 | 34.12 | 1.84 | 0.82 | | 0.26 | | | 99.92 |
| | 5 | 56.05 | 40.07 | 2.40 | 0.40 | 0.40 | None | 0.66 | | 99.98 |
| | 6 | 56.9 | 39.5 | 2.0 | 0.5 | 0.4 | 0.8 | None | | 100.2 |
| | 7 | 52.47 | 42.70 | 1.56 | 0.48 | None | 0.62 | 1.97 | | 99.80 |
| | 8 | 53.2 | 42.7 | 1.7 | Trace | 1.2 | 1.7 | None | | 100.7 |
| High alumina | 1 | 22.50 | 72.30 | 1.40 | 0.20 | 0.15 | 0.25 | 3.20 | | 100.00 |
| Diaspore | 1 | 33.54 | 59.64 | 1.76 | 0.54 | None | 1.55 | 2.34 | | 99.37 |
| | 2 | 22.7 | 70.8 | 1.8 | 0.1 | 0.3 | 0.9 | 3.7 | | 100.3 |
| Sillimanite | | 37.36 | 59.25 | 1.06 | 0.22 | None | | 1.57 | | 99.46 |
| Periclase[a] | | 1.50 | 0.24 | 0.06 | 1.40 | 96.60 | | | | 99.80 |
| Magnesia | 1 | 4.30 | 3.14 | 4.78 | 3.88 | 83.87 | | | | 99.97 |
| | 2 | 2.4 | 1.5 | 2.2 | 1.7 | 91.5 | | | | 99.33 |
| Kaolin | 1 | 63.9 | 30.0 | 4.0 | 0.1[b] | | 0.9 | 1.1 | | 100.0 |
| | 2 | 63.7 | 30.6 | 3.8 | 0.1[b] | | 0.9 | 1.1 | | 100.2 |
| | 3 | 51.40 | 44.60 | 0.90 | 0.35[b] | | 0.65 | 1.36 | | 99.26 |
| Chrome | 1 | 5.88 | 19.49 | 17.68 | 16.30 | | | | 40.65 | 100.00 |

[a] Henry G. Fisk and William J. McCaughey, "Equilibrium Studies in Systems Containing Magnesium Oxide, Iron Oxide, and Magnesium Aluminate," Ohio State University, Eng. Expt. Sta. *Bull.*, No. 70, p. 14 (1932).
[b] Calcium and magnesium oxides.

conditions; (3) full-sized brick were used and a temperature gradient existed between the face and the back of the brick; (4) the amount of slag and temperature was controlled; (5) the three types of slag action, abrasion, penetration, and chemical reaction were present; (6) qualitative and quantitative measurements were taken; and (7) a twenty-four hour test

FIG. 8.—Slagged brick compared with unslagged brick. Left to right: fire clay 5, high aluminous, diaspore 1, kaolin 1, fire clay 2, and fire clay 6.

at 2700°F and using 150 pounds of ash gave greater slag penetration than a one-year normal operation of an industrial installation.

## VII. Types of Refractories Tested

Five tests were made on various kinds of refractories. Table V gives the analyses of the brick tested, Table VI, a summary of the tests, and Table VII, the gain in chemical constituents of the slags from the original wood-ash content. The analyses of the brick were furnished by the manufacturers. In two preliminary tests not reported, only qualitative results were obtained.

TABLE VI

SUMMARY OF SLAG TESTS

| Test No. | Average temp. (°F)[a] | Total time (hr.) | Ash (lb.) | Refractory | Absorption (%) | Volume loss (%) |
|---|---|---|---|---|---|---|
| 1 | 2550 | 22.00 | 110 | Fire clay 3 | 7.0 | 33.4 |
| | | | | " 4 | 3.8 | 20.4 |
| | | | | " 5[b] | 2.0 | 8.4 |
| | | | | Kaolin 1 | 6.0 | 16.2 |
| | | | | Amphibole 1 | | Failed completely |
| | | | | Wash. talc 1 | | Badly eaten by the slag |
| 2 | 2750 | 20.25 | 154 | Fire clay 2 | 15.5 | 27.5 |
| | | | | Fire clay 5 | 7.5 | 14.3 |
| | | | | Fire clay 6 | 4.0 | 24.7 |
| | | | | Kaolin 3 | 7.5 | 1.5 |
| | | | | High alumina | 12.4 | 35.0 |
| | | | | Diaspore 1 | 9.0 | 18.2 |
| 3 | 2800 | 22.00 | 80 | Fire clay 2 | 19.1 | 26.0 |
| | | | | " (dense) | 1.9 | 8.4 |
| | | | | " 7 | 5.4 | 19.5 |
| | | | | " 8 | 4.8 | 12.0 |
| | | | | Kaolin 2A | 12.8 | 24.8 |
| | | | | Kaolin 2B[c] | 11.1 | 10.5 |
| | | | | Sillimanite | 8.0 | 4.3 |
| | | | | Diaspore 2 | 7.6 | 10.3 |
| | | | | Magnesia 2 | 6.0 | 5.1 |

[a] Average temperature after slagging was started.
[b] Stiff-mud processed.
[c] Kaolin 2A, refired to cone 18 (2714°F).

TABLE VII

GAIN IN SLAG CONSTITUENTS

| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | CaO | MgO | $K_2O$ | $Na_2O$ | $CO_2$ | Totals |
|---|---|---|---|---|---|---|---|---|---|
| Original ash | 16.15 | 4.22 | 5.81 | 34.25 | 0.82 | 9.02 | 4.79 | 24.65 | 98.79 |
| Slag No. 1 | 43.26 | 35.67 | 6.20 | 12.56 | 0.18 | 0.97 | 1.76 | | 100.60 |
| Gain | 27.11 | 31.45 | 0.39 | −21.69 | −0.64 | −7.74 | −2.89 | −24.65 | |
| Slag No. 2 | 54.42 | 16.67 | 10.69 | 14.35 | 0.65 | 2.32 | 1.75 | | 100.85 |
| Gain | 38.27 | 12.45 | 4.88 | −19.90 | −0.17 | −6.70 | −3.04 | −24.65 | |
| Slag* No. 3 | 45.00 | 36.71 | 6.80 | 9.95 | 0.09 | 1.08 | 1.90 | | 101.54 |
| Gain | 28.85 | 32.49 | 0.99 | −24.30 | −0.73 | −7.74 | −2.89 | −24.65 | |
| Av. slag | 47.56 | 29.68 | 7.90 | 12.29 | 0.31 | 1.46 | 1.80 | | 101.00 |
| Av. gain | 31.41 | 25.46 | 2.09 | −21.96 | −0.51 | −7.56 | −2.01 | −24.65 | |

A comparison of the slag analyses with those found in Table IV shows the similarity of the slags obtained from the slagging tests with many of those in industrial installations. The ash used in these tests was from wood that had been floated in sea water.

## VIII. Cone-Fusion Tests

The hogged-fuel ash was calcined at red heat to drive off the volatile matter, cooled, ground, and screened finer than 100-mesh. The screened material was added in increasing amounts to firebrick dust and cones were made of the mixtures which were fired on plaques with standard Orton cones. Two eutectics were found in most cases. Table VIII shows the minimum cone temperatures. It can be seen from this table that there is no correlation between the degree of slagging and the cone-fusion tests.

TABLE VIII

MINIMUM P.C.E. VALUES OF THE CONCENTRATION-TEMPERATURE DIAGRAMS OF BRICK AND WASTE-WOOD FUEL-ASH MIXTURES

Alumina content of the brick and the per cent volume loss

| Refractory | P.C.E. | Mixture | | Alumina (%) | Volume loss (%) |
|---|---|---|---|---|---|
| | | Ash | Refractory | | |
| Kaolin 1 | 1 | 50 | 50 | 30.0 | 16.2 |
| Fire clay 1 | 1 | 40 | 60 | 38.4 | 50.0 |
| | 1 | 80 | 20 | | |
| Fire clay 4 | 1 | 40 | 60 | 34.1 | 20.4 |
| Kaolin 3 | 3 | 50 | 50 | 44.6 | 1.5 |
| High alumina | 3.5 | 50 | 50 | 72.3 | 30.4 |
| | | 70 | 30 | | |
| Fire clay 2 | 4.5 | 50 | 50 | 51.9 | 28.8 |
| Diaspore 1 | 6.5 | 80 | 20 | 59.6 | 23.0 |
| | | 100 | 0 | | |
| Pure crystalline mullite[a] | 7.5 | 80 | 20 | 72.0 | |
| | | 90 | 10 | | |

[a] No samples of this material were used in the slagging tests.

## IX. Petrographic Examination

Petrographic thin-sections were made of the slagged brick to study the action of the slag on the brick face. Mullite and glass were found in all of the fireclay, diaspore, and kaolin brick. Several slags showed mullite throughout, while most of them showed it only at the slag-brick interface. The slag, in a few cases, had penetrated the pores to such an extent that pieces of brick were included in the slag. This was especially true of the diaspore brick.

## X. Relative Resistance Factor

Equation (1) was used to balance the variables of temperature, weight of slagging material, and time. Equation (2) was used to find the relative resistance of each refractory in terms of the least slagged refractory. The results obtained from equation (1) agreed with those from two tests in which the temperature and time were held constant.

$$\text{Resistance factor} = \frac{(\%\text{ volume loss})\,(K)}{(\text{hr.}-2.5)\,(\text{temp.})\,(\text{wt. ash})} \qquad (1)$$

$K$ = 1,000,000
Hr.–2.5 = time of test after slagging started
Temp. = average temperature after slagging started
Wt. ash = weight of slagging material

$$\text{Relative resistance} = \frac{\text{factor for given refractory}}{\text{smallest factor}} \qquad (2)$$

Table IX shows the relative resistance of the refractories as found from equation (2), the alumina-silica ratio, and the per cent absorption. The tentative ratings of refractory types are given in Table X.

TABLE IX

RELATIVE RESISTANCE OF REFRACTORIES IN THE SLAG TESTS, THEIR ALUMINA-SILICA RATIOS, AND PER CENT ABSORPTION

| Refractory | Relative resistance | Alumina-silica ratio | Absorption (%) | Refractory | Relative resistance | Alumina-silica ratio | Absorption (%) |
|---|---|---|---|---|---|---|---|
| Kaolin 3 | 1 | 0.9 | 7.5 | Kaolin 1 | 15 | 0.5 | 6.0 |
| Sillimanite | 5 | 1.4 | 8.0 | Fire clay 6 | 17 | 0.7 | 4.0 |
| Magnesia 2 | 6 | | 6.0 | Fire clay 2 | 18 | 1.1 | 15.5 |
| Fire clay 5 | 6 | 0.7 | 7.5 | Fire clay 4 | 19 | 0.5 | 3.8 |
| Fire clay 5 | 7 | 0.7 | 2.0 | Fire clay 7 | 22 | 0.8 | 5.4 |
| Fire clay (dense) | 10 | | 1.9 | High alumina | 23 | 3.2 | 12.4 |
| Diaspore 1 | 12 | 1.8 | 9.0 | Kaolin 2A | 28 | 0.5 | 12.8 |
| Diaspore 2 | 12 | 3.1 | 7.6 | Fire clay 2 | 30 | 1.1 | 19.1 |
| Kaolin 2B | 12 | 0.5 | 11.1 | Fire clay 3 | 30 | 0.4 | 7.0 |
| Fire clay 8 | 14 | 0.8 | 4.8 | Fire clay 1 | 38 | 0.7 | |

TABLE X

TENTATIVE RATING OF REFRACTORY TYPES

| Refractory | Tentative rating | Refractory | Tentative rating |
|---|---|---|---|
| Silicon carbide | 1 | Other fire clay and kaolin | 7 |
| Dense kaolin | 2 | Periclase | 8 |
| Sillimanite | 3 | Chrome | 9 |
| Dense magnesia | 4 | Silica | 10 |
| Dense fire clay | 5 | Amphibole | 11 |
| Diaspore | 6 | Washington talc | 12 |

No quantitative measurements were taken of the silicon carbide, periclase, chrome, silica, amphibole, or Washington talc. Their ratings, except the amphibole and talc, were taken from their relative resistance in the two preliminary tests.

## XI. Conclusions

The degree of slagging in a furnace burning waste wood and supplemented with oil firing is dependent on the following conditions: (1) the chemical composition of the brick, (2) the porosity and texture of the brick, (3) operation and temperature of the furnace, and (4) design of the furnace.

The recrystallized silicon carbide brick had less reaction with the ash than the other refractories. For the fireclay and diaspore type of refractory the porosity was of more importance than the alumina-silica ratio.

Localized zones of intense heat, such as the openings for air around the edge of the fuel bed, are generally slagged more than other portions of the furnace. The primary air entering along the edge of the fuel bed can be

diverted toward the center by placing a loose layer of brick on the grates next to the wall. Too small a combustion space not only causes heat losses but also slagging due to the reducing conditions and the localized "hot spots." The trouble found when oil is burned as an auxiliary to waste wood is believed to be due to the higher temperatures produced by the oil, thus increasing the fluidity and reactivity of the wood-ash slags.

**Acknowledgments** The writers desire to acknowledge their indebtedness to G. L. Rogers for his suggestion of the problem, to the various refractory companies supplying brick for the simulative service tests, to the owners of the various industrial plants for their coöperation in obtaining data on the slagging conditions in their plants, to George H. Krueger for his aid in obtaining data on the industrial installations, to C. R. Corey for his assistance with the analytical work, and to Hewitt Wilson for his supervision of the problem and the preparation of this paper.

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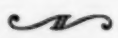

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# CERAMIC ABSTRACTS[1]

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Ross C. PURDY, Editor

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**Vol. 12** **August, 1933** **No. 8**

## Abrasives

**Device tests snagging wheels.** A. J. SANDORFF. *Abrasive Ind.*, **14** [5], 12 (1933).—A machine is described for testing the performance of experimental abrasive wheels simulating shop conditions. W.W.M.

**Finishing shouldered shafts.** R. E. W. HARRISON. *Abrasive Ind.*, **14** [5], 10–11 (1933).—Instead of undercutting the shaft at the shoulder to facilitate grinding, the grinding wheel is made thicker at the periphery than at the center to avoid grinding against the shoulder. This saves weakening the shaft by undercutting. W.W.M.

**Finishing threads accurately.** FRED B. JACOBS. *Abrasive Ind.*, **14** [4], 14 (1933).—An apparatus and its method of use for finishing threads accurately by grinding are described. The fixture is easily constructed and is designed to fit an engine lathe. W.W.M.

**Crankshafts ground from rough.** FRED B. JACOBS. *Abrasive Ind.*, **14** [5], 12 (1933).—J. describes fixtures required and procedure for economical finishing of single-throw crankshafts from rough stock. W.W.M.

**New grinding practice required.** ANON. *Abrasive Ind.*, **14** [5], 8 (1933).—The solution of the problem of grinding nitralloy bushings used on the axleshafts of four-wheel drive trucks included the redesigning of a grinder. The solution of this problem is discussed at length. W.W.M.

**Grinding joints of new cylinder liners.** ANON. *Neue Kraftfahrer-Ztg.*, Dec. 15, 1933; *Abrasive Ind.*, **14** [4], 21 (1933).—A novel method of lining cylinders consists of using thin sheets of Swedish steel rolled into sleeves and nitrided. The edges are not brazed or welded together but merely ground accurately and butted together. After being forced in place, only honing or polishing is necessary to form a hard, mirror-like finish. The joint can hardly be detected. W.W.M.

**Grinding strip steel rolls.** EDWARD S. HECK. *Abrasive Ind.*, **14** [4], 8 (1933).—The method of grinding rolls for finishing stainless steel strip is presented by H. The rough grinding and the production of the mirror effect are described. The importance of the latter is emphasized. The finishing mill life of the polished roll is about 8 hr. W.W.M.

**Cutting and trimming concrete slabs.** A. B. LAING. *Abrasive Ind.*, **14** [4], 17 (1933).—L. describes apparatus and method of use in sawing asphalt impregnated concrete slabs. Abrasive coping wheels are used and the result is a saving in cost over previous methods. W.W.M.

**Polishing velocipede parts.** ANDREW V. RE. *Abrasive Ind.*, **14** [4], 13 (1933).—R. outlines the method of handling work rapidly and gives the practice employed in making up velocipede wheels. The practice outlined can be followed for similar articles. W.W.M.

**Grinding as aid to astronomers.** F. A. WESTBROOK. *Abrasive Ind.*, **14** [4], 12 (1933).—The accurate grinding of the 60-lb. steel rails supporting the revolving dome of the Mount Wilson Observatory and the grinding apparatus employed are described. W.W.M.

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[1] The abbreviation (*C.A.*) at the end of an abstract indicates that it was obtained from *Chemical Abstracts* by coöperative agreement.
The bold-face number following the journal name is the volume, the issue number is in brackets, followed by the page numbers, then the year in parentheses.

PATENTS

**Abrasive and holder therefor.** W. G. DUNN. U. S. 1,908,697, May 16, 1933.

**Valve grinding machine.** J. R. TURNER. U. S. 1,908,937, May 16, 1933. F. O. ALBERTSON (Albertson & Co., Inc.). U. S. 1,909,446, May 16, 1933.

**Valve grinder.** WILLIAM BARBER. U. S. 1,908,946, May 16, 1933.

**Shears grinder.** HENRY YERKEY. U. S. 1,909,033, May 16, 1933.

**Building up of machine tools, especially grinding machines.** CARL KRUG. U. S. 1,909,110, May 16, 1933.

**Hydraulic operating system for machine tools.** E. P. BURRELL (Warner & Swasey Co.). U. S. 1,909,165 and 1,909,166, May 16, 1933.

**Gear grinder, etc.** ORLANDO GARRISON (Pratt & Whitney Co.). U. S. 1,909,398, May 16, 1933.

**Rotary grinding machine.** E. B. GARNER (Hanchett Mfg. Co.). U. S. 1,909,614, May 16, 1933.

**Grinding machine.** F. G. MUSHENO (Allegheny Steel Co.). U. S. 1,909,705, May 16, 1933. R. A. HEALD (Heald Machine Co.). U. S. 1,909,953, May 23, 1933. V. K. BOYNTON (Pittsburgh Plate Glass Co.). U. S. 1,910,234, May 23, 1933. C. R. DAHLIN (Heald Machine Co.). U. S. 1,911,266, May 30, 1933. R. A. COLE AND A. G. BELDEN (Norton Co.). U. S. 1,911,552, May 30, 1933. W. F. FRASER (Norton Co.). U. S. 1,911,889 and 1,911,890, May 30, 1933.

**Abrasive product and method of making.** E. E. NOVOTNY (John S. Stokes). U. S. 1,909,784, May 16, 1933. An abrasive composition comprises abrasive grains, a gum accroides resin, and a hardening reagent therefor.

**Process of making abrasive materials.** K. C. NICHOLSON (Carborundum Co.). U. S. 1,910,444, May 23, 1933. In the manufacture of abrasive granules, the steps comprise mixing the abrasive granules with a non-agglomerating slurry of vitrifiable material and heating the mixture to vitrify the coatings of vitrifiable material on the respective granules.

**Saw grinding machine.** J. E. JIRKA. U. S. 1,909,832, May 16, 1933.

**Sharpening machine.** W. E. NICKERSON (Gillette Safety Razor Co.). U. S. 1,909,883, May 16, 1933.

**Sharpening machine for curved blades.** W. E. NICKERSON (Gillette Safety Razor Co.). U. S. 1,909,884, May 16, 1933.

**Abrasive article of ceramic bonded crystalline alumina granules.** L. H. MILLIGAN AND C. H. QUICK (Norton Co.). U. S. 1,910,031, May 23, 1933. An abrasive article comprises crystalline alumina granules bonded by a vitrified ceramic bond of the glassy type, characterized in that the ceramic mixture forming the bond contains a highly plastic clay which renders the bond moldable in the raw condition and an added flux which causes the bond to mature into a substantially glassy, viscous, liquid condition at a temperature below Orton cone 13 and unite the granules into an integral body, the bond containing insufficient slip clay or iron compounds to cause material swelling of the article during the firing operation, and the iron content being less than 1% by weight of the total bond.

**Abrasive reamer.** C. W. TYDEMAN (A. Oberholtz, Jr.). U. S. 1,910,658 and 1,910,659, May 23, 1933.

**Appliance for razor blade sharpening devices.** ROBERT NAVARRE. U. S. 1,910,710, May 23, 1933.

**Grinding and polishing machine.** I. J. HASKEL. U. S. 1,910,897, May 23, 1933.

**Machine for precision grinding.** R. A. COLE AND A. G. BELDEN (Norton Co.). U. S. 1,911,553, May 30, 1933.

**Multiple chucking machine.** A. J. LEWIS (Baird Machine Co.). U. S. 1,911,632, May 30, 1933.

**Grinder speed control.** WALTER STUMPF (Marschke Mfg. Co.). U. S. 1,911,857, May 30, 1933.

**Die lapping machine.** G. H. SITTNER (General Electric Co.). U. S. 1,912,016, May 30, 1933.

**Cylinder grinding tool.** F. G. WACKER AND H. W. ZIMMERMAN (Automotive Maintenance Machinery Co.). U. S. 1,912,025, May 30, 1933.

**Grinding wheel.** A. J. DOERMANN (Titan Abrasives Co., Inc.). U. S. 1,912,069, May 30, 1933.

**Abrasive disk.** A. J. DOERMANN (Titan Abrasives Co., Inc.). U. S. 1,912,070, May 30, 1933.

**Method and apparatus for lapping gears.** A. C. PAGE (Detroit Trust Co.). U. S. 1,912,216, May 30, 1933.

**Device for dressing grinding wheels.** WILLIAM SHOTEY. U. S. 1,912,410, June 6, 1933.

**Buffing machine.** W. T. MINETT (United Shoe Machinery Corp.). U. S. 1,912,491, June 6, 1933. N. H. KNOWLTON (United Shoe Machinery Corp.). U. S. 1,912,528, June 6, 1933.

**Apparatus for polishing articles.** H. L. VANDEVORT (Standard Steel Specialty Co.). U. S. 1,912,552, June 6, 1933.

**Saw grinding and setting machine.** G. E. TRIMBLE. U. S. 1,913,354, June 6, 1933.

**Apparatus for grinding cylindrical and tapered bodies.** S. J. MORTIMER, W. A. W. EVANS, AND F. POLLARD & CO. (BEARINGS), LTD. Brit. 391,243, May 3, 1933.

**Grinding of cylinder bores and apparatus therefor.** H. J. J. HUDSON. Brit. 391,268, May 3, 1933.

**Machine for grinding lathes, etc.** SCHIESS-DEFRIES AKT.-GES. Brit. 391,357, May 3, 1933.

**Machine for grinding knife blades.** A. V. HAGUE, JR. Brit. 391,447, May 10, 1933.

**Hydraulically-operated automatic lathes.** W. W. TRIGGS (Warner & Swasey Co.). Brit. 391,456, May 10, 1933.

**Processes for producing polished surface effects.** L. T. GMACH. Brit. 391,488, May 10, 1933.

**Machine for sharpening scissors and other edge tools.** G. STOKES. Brit. 391,719, May 10, 1933.

**Abrasive tools and papers.** I. G. FARBENIND. A.-G. Fr. 740,640, Aug. 1, 1932. Grains of abrasive material are mixed with binders containing rubber derivatives, the thermoplasticity of which is reversible, *i.e.*, with products which result from the transformation or degradation of rubber, and which, after being heated, return to their initial physical state. The products may be obtained by a simple heating of rubber to 250 to 280°, with or without solvents, or by a chemical treatment with $H_2SO_4$, sulfoacetic acid, $CCl_3COOH$, $POCl_3$, or $SbCl_5$. (*C.A.*)

**Material for sharpening cutlery.** SYÛZÔ INOUE (Bunzaburô Banno). Japan. 94,207, Jan. 19, 1932. The material is a mixture of finely powdered alkali aluminate, glycerol, oil, or fat and oxides of Al, Cr, or Fe. (*C.A.*)

## Art and Archeology

**Producing a chrome-tin mat glaze.** GEORGE BLUMENTHAL, JR. *Ceram. Ind.*, **20** [5], 222 (1933).—B. gives procedures and results of experiments with the production of a chrome-tin mat glaze. The glaze and its color are difficult to control in firing. Three sources of chromium oxide were used in making up the trial stains. The range of maturity of the glaze used was between cone 04 and cone 1. Tabulated data are presented. W.W.M.

**White translucent glass tableware.** MACBETH-EVANS GLASS CO. *Ceram. Ind.*, **20** [5], 221 (1933).—The design of a tea set in white translucent glass that has an opalescent tinge is described with a photographic illustration. W.W.M.

**Old English glass. No. 41. Restoration glassmakers.** F. BUCKLEY. *Glass*, **10** [4], 146–47 (1933).—One of the most difficult periods to illustrate in the history of fine English glassmaking lies between 1660 to 1674. Examples of fine glass made in England at this time are scarce and difficult to identify. Four illustrations are presented. For No. 40 see *Ceram. Abs.*, **12** [7], 251 (1933). G.R.S.

**Rare Chelsea jug.** ANON. *Pottery Glass Rec.* [Eng.], **15** [5], 142 (1933).—An extremely rare Chelsea "Goat and Bee" jug of 1751 with the triangular impressed mark has been presented to the Birmingham Museum and Art Gallery in England. M.V.K.

**Monte Alban: richest archeological find in America.** ALFONSO CASO. *Nat. Geog. Mag.*, **62**, 487–512 (1932); see abstract by Lodge, *Ceram. Abs.*, **12** [3], 92 (1933). H.H.S.

**Progress of archeology.** ANON. *Discovery*, **14**, 97 (1933).—Outstanding finds at Athens, Corinth, Troy, and Persepolis are summarized. H.H.S.

**Magnificent discoveries at Persepolis.** ERNST HERZFELD. *Illus. London News*, **182**, 401–406, 453–55 (1933).—The discoveries of the Chicago Oriental Institute Expedition directed by H., under the general direction of J. H. Breasted, are described as the greatest in archeology for past years. Illustrated with photographs. H.H.S.

**Hermoupolis.** SAMY GABR. *Illus. London News*, **182**, 310–11 (1933).—Whole streets of Greece-Egyptian buildings have been excavated by Egyptian university men. H.H.S.

**Neolithic pottery in Malta.** C. G. ZAMMIT. *Illus. London News*, **182**, 339 (1933).—A stone age sanctuary at Imjar has yielded pottery of two types. H.H.S.

**Sung ware.** FRANK DAVIS. *Illus. London News*, **182**, 360 (1933).—Three photographs of Sung dynasty ware (960 to 1280 A.D.) are presented. H.H.S.

**Death of famous pottery artist.** ANON. *Pottery Glass Rec.* [Eng.], **15** [5], 138–39 (1933).—The biography of the versatile artist, Frederick Alfred Rhead, is given. M.V.K.

**Spode bicentenary.** ANON. *Pottery Gaz.*, **58** [670], 482–84 (1933); for abstract see *Ceram. Abs.*, **12** [7], 251 (1933). E.J.V.

BOOK

**Pottery: The Finger-Built Methods.** HENRY AND DENISE WREN. Isaac Pitman and Sons, London. 5s net. Reviewed in *Pottery & Glass Rec.* [Eng.], **15** [4], 100 (1933).—This little book is a serious attempt to impart knowledge of some bygone primitive processes with a view of stimulating individual effort on distinctive lines. Having in view the youthful initiate rather than the experienced workers in clayware, full explanations are given of materials and equipment required and careful attention is paid to the selection of the proper clay and glazes and ways of working them. Apart from the insight gained of the making and firing of pots, figurines, and animals, as well as tile in earthenware bodies, there is much of worth in the illustrations depicting ancient Mexican, Peruvian, Nigerian, and other early ceramic ware. M.V.K.

PATENTS

**Design for cooking stove.** H. H. FLEER (Eureka Steel Range Co.). U. S. 89,881, May 16, 1933. M. G. KLEMME (Eagle Foundry Co.). U. S. 89,966, May 23, 1933. W. F. ROGERS (Crown Stove Works). U. S. 90,085, June 6, 1933.

**Design for jar.** E. W. FUERST (Owens-Illinois Glass Co.). U. S. 89,885, May 16, 1933. FRASIER SMITH (Hazel-Atlas Glass Co.). U. S. 89,976, May 23, 1933.

**Design for glass globe.** K. A. STALEY (Gillinder Bros., Inc.). U. S. 89,927, May 16, 1933.

**Design for range.** G. D. WILKINSON AND E. D. PELLEGRIN (Cribben & Sexton Co.). U. S. 89,981, May 23, 1933.

**Design for dish.** E. B. BEDFORD AND M. G. PARKER (Oneida Community, Ltd.). U. S. 89,983 and 89,984, May 23, 1933.

**Design for beer mug.** IRVING FLORMAN. U. S. 90,022, May 30, 1933.

**Design for bottle.** E. W. FUERST (Owens-Illinois Glass Co.). U. S. 90,023, May 30, 1933, and U. S. 90,069, June 6, 1933. L. P. GREY (Hazel-Atlas Glass Co.). U. S. 90,029, May 30, 1933. W. J. POPP. U. S. 90,047, May 30, 1933.

**Design for fish bowl.** SOOVIA JANIS (Samuel J. Carnes). U. S. 90,032, May 30, 1933.

**Design for cabinet type gas range.** HENRY LANGE (Quincy Stove Mfg. Co.). U. S. 90,035, May 30, 1933.

**Design for glass jar.** F. J. PETTY (Ball Bros. Co.). U. S. 90,045, May 30, 1933.

**Design for stein.** WALTER WATLING. U. S. 90,046, May 30, 1933.

**Design for tumbler.** F. S. BARBIERS (Hocking Glass Co.). U. S. 90,060, June 6, 1933. T. J. PIAZZOLI (Capstan Glass Co.). U. S. 90,082, June 6, 1933.

**Design for combined bottle and stopper.** F. R. TOURTOIS (Coty, Inc.). U. S. 90,093, June 6, 1933.

**Transferring designs.** WINTHROP S. LAWRENCE (Kaumagraph Co.). U. S. 1,893,626, Jan. 10, 1933. For transferring a design consisting of a film of soluble material such as a nitrocellulose composition intermixed with coloring matter and carried on a base such as paper, the base is immersed in a transfer liquid comprising a plurality of liquids such as Et lactate and benzine in which the film has a varying solubility (the more active solvent having the higher boiling point) for a sufficiently short time to prevent the film from being dissolved or "running," and the transfer design is then applied directly to the surface to be marked after permitting the liquid having the lower boiling point to evaporate until the transfer can be utilized without any substantial "running." See also U. S. 1,827,591, Oct. 13, 1931. (*C.A.*)

**Decalcomania adhesive.** R. H. PRICE (Glue Research Corp.). U. S. 1,909,719, May 16, 1933. As a new composition of matter, a decalcomania adhesive comprises substantially 13.5% glue, 28% water, 7.3% butanol, 9.7% toluol, 26.8% alcohol, and 14.7% Turkey red oil.

**Method and means for printing on glass, etc.** C. L. MENDOZA. Brit. 391,992, May 17, 1933.

**Decoration of ceramic products, glass, enameled iron, etc.** E. R. Box, N. W. White, and Johnson, Matthey & Co., Ltd. Brit. 392,222, May 24, 1933.

## Cements

**Chemistry of Portland cement in complex chemical representation.** Lennart Forsén. *Zement*, **22** [6], 73–77; [7], 87–91; [8], 100–102 (1933).—F. uses the Werner coördination method of portraying complex inorganic compounds and makes many useful applications to the various compounds capable of being formed during the hydration of setting of Portland cement. *E.g.*, tricalcium aluminate may crystallize with 6, 12, or 18 mols of water which may be written as anhydride, $Ca_3[Al(OH)_6]$, the diaquo salt, $[Ca(OH_2)_2]_3\,[Al(OH)_6]$, and the tetraquo salt, $[Ca(OH_2)_4]_3\,[Al(OH)_6]_2$, respectively. All three remain as the hexahydrate after drying in a desiccator; $2CaO{\cdot}Al_2O_3{\cdot}7H_2O$ and $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$, which change on drying to $5H_2O$ and $7H_2O$, respectively, are also described. Tricalcium aluminate forms a series of double salts with other calcium salts including two with the sulfate and one each with chloride, bromide, iodide, nitrate, and chlorate. A series of basic calcium salts is discussed including CaO, $CaX_2{\cdot}3H_2O$, which dries to a monohydrate, and $3CaO$, $CaX_2{\cdot}15H_2O$, which dries to a trihydrate. A well-graded series ranging from tricalcium silicate, 3:1, hillebrandite, 2:1, through afwillite, 3:2, to plombierite, 1:1 occurs among the calcium silicates. The hydration and hydrolyzing of trisilicate in Portland cement may pass through this series under certain conditions. Tricalcium silicate reacts vigorously with aluminates and this is blamed for the flash setting of cements. The aluminate forms a protective coating around the silicate slowing down further hydration and preventing swelling of the gel. When gypsum is present the insoluble double salt is precipitated and the silicate proceeds to hydrate and swell to form a gel. See also *Ceram. Abs.*, **12** [5], 204 (1933). M.V.K.

**Influence of aluminate and ferrites on the properties of Portland cement.** J. Konarzewski. *Przemysl Chem.*, **16** [8–9], 186–88 (1932); abstracted in *Chim. & ind.*, **29** [4], 852 (1933); see also *Ceram. Abs.*, **12** [4], 140 (1933). M.V.K.

**Action of lime on silica in its relation to the setting of Portland cement.** A. J. P. Van der Burgh. *Chem. Weekblad*, **29** [43], 616–18 (1932); abstracted in *Chim. & ind.*, **29** [4], 854 (1933).—The action of lime on silica in movement or at rest produces different results. Small additions of lime were added to water containing 10 g. gelatinous silica; after each addition, the solution was shaken for 24 hr. The analysis of the liquid floating on the surface permits the calculation of the amount of lime fixed by silica. The ratio $CaO{:}SiO_2$ approaches unity, while the lime content of the liquid remains constant. A combination $CaO{\cdot}SiO_2$ which may adsorb a part of the lime surplus, 0.4 mol. approximately, is thus formed. The voluminous body does not possess any cohesion. Some saturated limewater was added to gelatinous silica to study the phenomena occurring in a liquid at rest. The silica became covered with a white solid coat of 0.05 mm. thickness which is isotropic in polarized light. The composition is approximately $CaO{\cdot}SiO_2$. When using nondialyzed silica gel, a layer of the liquid is seen between the gel and the calcium silicate. This liquid is formed because calcium silicate is impermeable to lime; every lime molecule penetrating this surface is immediately fixed in the form of a silicate. In nondialyzed silica there are ions of sodium and of hydroxyl which may diffuse through the calcium silicate layer rendering the liquid alkaline so that some of the gel is dissolved. M.V.K.

**Recast analysis and its relation to the chemistry of Portland cement. X. Computation of Portland cement raw mixtures.** Louis A. Dahl. *Rock Prod.*, **36** [4], 28–29 (1933).—D. continues with illustrations of computations of Portland cement raw mixtures from several components, using equations and charts. For Part IX see *Ceram. Abs.*, **12** [7], 253 (1933). W.W.M.

**Action of media with an alkaline reaction on the crystallization of aluminates of lime and on the setting of aluminous cements.** M. Séailles. *Compt. rend. acad. Sci.*, **195** [16], 662–64 (1932); abstracted in *Chim. & ind.*, **29** [4], 854 (1933); for abstract see *Ceram. Abs.*, **12** [4], 141 (1933). M.V.K.

**Researches on nature and progressive action of pozzuolanas.** M. Feret. *Rev. mat. constr. trav. pub.*, No. 281, pp. 41–44; No. 282, pp. 85–92 (1933). M.V.K.

**Cement coloring.** Anon. *Rev. mat. constr. trav. pub.*, No. 283, pp. 132–33 (1933).—Investigations made by the Society of French Cements showed that the coloring action of metallic salts and notably iron salts is possible only in the presence of a sufficient quantity of magnesia. When the magnesia content of the clinker reaches 1%, the

coloring effect of additions of metallic salts becomes quite distinct; this effect becomes irregular when the magnesia content exceeds 2%. Dolomite and dolomitic limestone rich in magnesia can be used. M.V.K.

**Method for manufacturing synthetic porcelain.** ANON. *Ind. chimique*, **20** [331], 306 (1933).—A new method permitting the manufacture of plastic materials similar to porcelain is described. These plastic materials are obtained by mixing products like kaolin, talc, cryolite, powdered aluminum, etc., with chlorinated naphthalenes. One of the methods employed is as follows: 20 parts of talc and 80 parts of chloronaphthalene, containing 50% chlorine, are mixed and stirred at 120°C; the product obtained is similar to porcelain but it becomes soft when heated. If the proportion of talc is doubled, the product is harder to work although it can be worked in presses. Colored products may be obtained in the same way by adding pigments and coloring matter. M.V.K.

BOOK

**Chemistry of Cements.** (Chemie der Zemente.) K. E. DORSCH. Julius Springer, Berlin, 1932. 277 pp. Unbound 23.50 Rm., bound, 25.00 Rm. Reviewed in *Chim. & ind.*, **29** [4], 856 (1933).—In this book D. gives the chemical and physicochemical problems of cement. After a rational classification of mortars and a study of raw materials, a detailed review of all binary and ternary systems present in cement is given. The second part deals with the theory of manufacture. The work is completed by a study of hardening and corrosion. M.V.K.

PATENT

**Method for improving cement and cement mortar, and product thereof.** WALTER KIRCHNER (Chemische Fabrik Grunau, Landshoff & Meyer Akt.-Ges.). U. S. 1,910,297, May 23, 1933. A method for improving the properties of hydraulic binding media comprises adding sulfohydrocyanic acid to hydraulic binding media before hardening.

## Enamels

**Some sheet-iron ground-coat reboil and bond studies using several enameling stocks.** H. E. EBRIGHT, C. D. CLAWSON, AND J. T. IRWIN. *Jour. Amer. Ceram. Soc.*, **16** [7], 305–11 (1933).

**Results of some shop tests on reboiling.** F. R. PORTER. *Jour. Amer. Ceram. Soc.*, **16** [7], 312–14 (1933).

**Effect of sodium aluminate on consistency and acid resistance of some acid-resistant enamels.** G. H. MCINTYRE, J. T. IRWIN, W. K. CARTER, AND R. M. KING. *Jour. Amer. Ceram. Soc.*, **16** [7], 315–18 (1933).

**Effect of zinc oxide on sheet-iron cover-enamel properties.** L. D. FETTEROLF. *Jour. Amer. Ceram. Soc.*, **16** [7], 319–24 (1933).

**X-ray investigation of the opacifying compounds present in sheet-iron cover enamels.** A. I. ANDREWS AND J. P. BREEN. *Jour. Amer. Ceram. Soc.*, **16** [7], 325–27 (1933).

**Thermal expansion of sheet-iron ground-coat enamels.** A. I. ANDREWS AND R. K. SMITH. *Jour. Amer. Ceram. Soc.*, **16** [7], 328–37 (1933).

**Reliability of cross-bend, impact, and reflectivity data obtained from various sizes of test pieces.** G. H. MCINTYRE, J. T. IRWIN, AND M. G. AMMON. *Jour. Amer. Ceram. Soc.*, **16** [7], 338–43 (1933).

**Enameling copper and copper alloys.** ANON. *Emailletech. Monats-Blätter*, **9** [5], 35–38 (1933).—The enameling of copper and copper alloys has long been practiced in the jewelry business where it is done by fusing the colored enamels in cells of the copper or alloy so that the expansivity or adhering qualities of the enamel have no great importance. In copper alloys containing zinc, the zinc hinders the adherence of the enamel due to its oxidizing during the firing and spoiling the adhering surface. A patent, Ger. 569,095, has been granted for a process whereby copper or alloys containing not less than 95% copper can be enameled. The surface is prepared for enameling by a treatment in a nitric acid bath, then a nitric acid-sulfuric acid bath, followed by a sandblasting treatment. The enamel is sprayed on and must be of such a composition that the opacifying agents are at a minimum and are completely fused when the enamel melts at a fairly high temperature. A typical enamel formula consists of 45.5% $SiO_2$, 8.0% $K_2O$, 14% $Na_2O$, 19.5% $B_2O_3$, 6.5% $Al_2O_3$, and 6.5% $CaF_2$. E.J.V.

**Manufacturing enameled sanitary ware. III. Acid-resisting enamel.** LOUIS

WOLFF. *Better Enameling*, **4** [4], 18 (1933).—W. compares manufacturing and inspecting procedure for acid-resisting and ordinary enamels. Acid-resisting enamels are harder, more lustrous, and of closer texture. Their production is slower and, in grading the ware, minor irregularities are allowed in first-class ware. Handling of the ware after it leaves the factory is discussed. For Part II see *Ceram. Abs.*, **12** [7], 255 (1933). W.W.M.

**Important improvements of enameled commodities.** H. G-GE. *Emailletech. Monats-Blätter*, **9** [5], 38 (1933).—An improved enamel is obtained by adding metallic silicon, silicides of the heavy metals, or silicon carbide. These enamels resist great temperature changes and possess great mechanical strength and hardness. The silicon or silicides are purified with acid prior to adding them to the enamel batch in the new process. For enameling pots and kettles which have to stand great temperature changes, an addition of 30% iron silicide containing 85% silicon, is used. E.J.V.

**Producing grained and marbleized finishes in porcelain enamel.** D. B. WALTERS. *Better Enameling*, **4** [4], 13 (1933).—W. describes two methods of wood graining and marbleizing porcelain enamel. The equipment necessary is listed. Variations of the methods are given. Illustrated. W.W.M.

**Basic materials for production of enamel.** MAURICE DELANGRE. *Céram. Verrerie*, pp. 207–209, 267–68, 327–28 (1932).—Essential constituents of enamel are discussed and analyses of various feldspars are given. Pipe clay is considered and the functions of $B_2O_3$, borax, $K_2CO_3$, and $Na_2CO_3$ in enamels are discussed. See following abstract. (*C.A.*)

**Raw materials for enamels.** MAURICE DELANGRE. *Céram. Verrerie*, **843**, 434, 503–504 (1932). (*C.A.*)

**Increasing white opacity.** TECHNOCHEMIE AKT.-GES. *Emailletech. Monats-Blätter*, **9** [4], 27–28 (1933).—A full description of a patented (*Ceram. Abs.*, **12** [6], 217 (1933)) process for increasing the opacity of white enamel, using tin oxide as the opacifier, by repeated heating as in a tunnel kiln with alternate heating and cooling zones, is given. A smaller amount of opacifier is required with this treatment, thus decreasing enamel costs. E.J.V.

**Effects of water vapor on porcelain enamel during firing.** H. E. EBRIGHT AND G. H. MCINTYRE. *Enamelist*, **10** [6], 11–13 (1933).—The authors give, with illustrations, the effects of water vapor on porcelain enamel during firing of both cast-iron and sheet-iron enamels. Tests showed that burning furnace atmospheres even when only partially saturated with water vapor during the firing of cast-iron enamels produce bad blistering and a greasy luster. The same condition for sheet-steel enamels produces bad "boiling," copperheading, and blistering, the luster being unaffected. W.W.M.

**Porcelain enamel practical for radiant type radiators.** ERIE ENAMELING CO. *Ceram. Ind.*, **20** [5], 223–24 (1933).—Radiant type radiators are being set into the walls of homes between the studding. It has been found practicable to enamel these radiators. W.W.M.

**Processes for decorating enamel vessels.** GUSTAV HEUBACH. *Emailletech. Monats-Blätter*, **9** [4], 29–30 (1933); for patent see *Ceram. Abs.*, **11** [10], 515 (1932). E.J.V.

**Adequate venting of enameling furnaces.** W. G. LESLIE. *Better Enameling*, **4** [4], 9 (1933).—Furnaces are often designed for greatest economy at the expense of best operating conditions. A furnace having too small a flue area is cited and a simple method for eliminating furnace gases is described. W.W.M.

### PATENTS

**Cooking stove.** M. G. KLEMME (Eagle Foundry Co.). U. S. 1,910,255, May 23, 1933.

**Sandblast gun.** L. D. PEIK (American Foundry Equipment Co.). U. S. 1,910,497, May 23, 1933.

**Rack for supporting enameled ware.** CHARLES KAPNER. U. S. 1,910,841, May 23, 1933.

**Tray and method of making.** G. W. FITZ GERALD (Beacon Enameled Products, Inc.). U. S. 1,910,888, May 23, 1933.

**Enamels and glazes.** IGNAZ KREIDL. Ger. 569,436, Sept. 1, 1929. In producing white opaque enamels and glazes with the aid of a substance which evolves a gas during the firing, the opacity is controlled by varying the size, number, and distribution of the gas bubbles. This is effected by increasing or reducing the degree of dispersion and (or) the adsorptive capacity of the clay or other adsorbent for the gas-evolving agent according to whether an increased or a decreased opacity is desired. (*C.A.*)

## Glass

**Sorption of water vapor by glass.** E. P. BARRETT AND A. W. GAUGER. *Jour. Phys. Chem.*, **37** [1], 47–51 (1933).—A test of the rectilinear character of the logarithmic form of the sorption isotherm for the system water vapor–glass was made over a range of relative humidities from $10^{-3}$ to $3 \times 10^{-2}$. The results agree closely with the precise measurements of Frank and indicate that his isotherm may be extrapolated to include pressures of the next higher order of magnitude. G.R.S.

**Physical and chemical methods for testing glasses in industrial laboratories. III.** F. H. ZSCHACKE. *Glashütte*, **63** [1], 9–10; [2], 27–28; [3], 43–44; [5], 80–81; [7], 111–12; [10], 169–71 (1933).—Z. discusses in detail the following methods for testing glass: I. Testing glass for its thermal resistance: (*a*) glass plates, (*b*) hollow bodies; II. Chemical methods for investigating glass (qualitative methods): (1) methods using pigments as indicators (phenolphthalein, methyl-red, and bromo-thymol-blue methods), (2) precipitation methods (narcotin hydrochloride and strychnine methods), (3) efflorescence tests: (*a*) hydrochloric acid test of Weber, (*b*) spot sensitiveness according to Zschimmer; III. Quantitative methods: (1) investigations on glass bodies, (*a*) weathering method of Mylius, (*b*) extraction method of Mylius, (*c*) testing bottle glass according to Keppeler, Jebsen-Marwedel, and Becker, (*d*) dissolving tests of Weber and Sauer; (2) testing of glass grit, (*a*) standard grit test of the German Glass Technical Society, (*b*) rapid methods of Fischer, Tepohl, and Kraft, (*c*) sensitiveness to spots of Heinrich and Tepohl. For Part II see *Ceram. Abs.*, **12** [5], 184 (1933). M.V.K.

**Sulfate a rational flux in the glass industry.** ANON. *Glashütte*, **63** [6], 93–94 (1933). M.V.K.

**Interchangeable and standard taper ground glassware.** W. T. LEVITT. *Ind. Eng. Chem., News Ed.*, **10**, 268 (1932).—U. S. makers have agreed to use standard tapers (9 sizes) for ground-glass joints. A certified set of master tools is obtainable from the Bureau of Standards. Ware conforming to specifications carries the mark "T" with the letter "S" through it plus the size number. (*C.A.*)

**Raw materials for glass manufacture.** ANON. *Glashütte*, **63** [6], 94–95 (1933).—Raw materials and products exhibited at the meeting of the German Glass Technical Society, held in Berlin, included glass objects colored by rare earths and products manufactured from "Bikorit," an electrothermally melted alumina. Its $Al_2O_3$ content is 99.2 to 99.5% and the melting point is at 2050°. Other raw materials and companies producing them are mentioned. M.V.K.

**Study of the volatilization losses from glasses containing potash and silica.** E. PRESTON AND W. E. S. TURNER. *Glass*, **10** [3], 104 (1933); see also *Ceram. Abs.*, **12** [6], 218 (1933). G.R.S.

**Notes on the manufacture of special glasses. XIV. Homogeneity of colorless glasses.** ANON. *Glass*, **10** [4], 140–45 (1933).—Methods for the detection and examination of inhomogeneity in glass are outlined as follows: (1) significance of striae, (2) ordinary visual examination, (3) examination by the immersion method, (4) optical methods, and (5) detection of stresses due to inhomogeneity. For Part XIII see *Ceram. Abs.*, **12** [7], 257 (1933). G.R.S.

**Magnesium oxide as a substitute for sodium oxide in mechanized manufacture of glass.** I. I. KITAIGORODSKII AND N. S. BREGMAN. *Keram. i Steklo*, **9** [2], 23–26 (1933).—The question of a partial replacement of sodium oxide by magnesium oxide present in dolomite for the composition of glasses manufactured mechanically was investigated. Magnesium glasses with additions of alumina were studied also. Dolomite of the average composition, 0.66% $SiO_2$, 0.82% $Al_2O_3$, 0.50% $Fe_2O_3$, 30.9% CaO, 20.24% MgO, was used. The most important properties were determined. It was found that a partial replacement of sodium oxide by magnesium oxide is possible and desirable. Compositions for the mechanized manufacture of window and bottle glass which would permit the reduction of the sodium oxide content by 20 to 25% are given. The maximum quantity of magnesium oxide for replacing sodium oxide is from 3 to 3.5%. The lowering of the sodium oxide content and its partial replacement by magnesium oxide will improve the quality of the glass, particularly its thermal stability, and the working properties of the glass. M.V.K.

**Character, significance, and requirements of safety glass. III.** C. H. ZEFER. *Glashütte*, **63** [1], 5–8; [5], 75–80; [9], 151–55 (1933).—S. discusses in detail German and foreign patents dealing with safety glass and technical literature devoted to it. For Part II see *Ceram. Abs.*, **12** [6], 220 (1933). M.V.K.

**Hydraulic presses for making safety glass.** T. PESCH AND L. LANSBERG. *Kunsti-*

*stoffe*, **22**, 124 (1932).—Presses with several openings have the following advantages: (1) they are closed while heated and effect a uniform heating of all layers; (2) they lose less heat through conduction as they are smaller; (3) hot water, steam, or electricity can be used for heating; and (4) a small number of simple mercury thermometers can be used instead of expensive thermocouples. It is advisable to use two sizes of presses for windshields and side windows. Five layers are about the limit. J.G.T.

**Should safety glass have one or more layers?** M. VOGT. *Kunststoffe*, **22**, 202–204 (1932).—"Sekuritglas," a one layer "safety" glass produced by a method which leaves high mechanical strains between the inner and outer layers of the pane, is shown to be far inferior to ordinary 3-layer safety glass in every respect. See also abstract by Blume, *Ceram. Abs.*, **12** [7], 257 (1933). (*C.A.*)

**Notes on toughened plate glass.** JAMES MEIKLE. *Pottery Glass Rec.* [Eng.], **15** [5], 148 (1933); see also *Ceram. Abs.*, **12** [7], 258 (1933). M.V.K.

**Comments on cyanite as a glass material.** J. H. WEIS. *Ceram. Ind.*, **20** [5], 235 (1933).—W. comments on the article "Cyanite, a new glass material" (*Ceram. Abs.*, **12** [7], 259 (1933)) and concludes that the refractoriness of cyanite is the chief obstacle to its use. W.W.M.

**Application of statistical methods to the quality control of manufactured products.** BERNARD P. DUDDING. *Glass*, **10** [3], 103 (1933); see also *Ceram. Abs.*, **12** [6], 221 (1933). G.R.S.

**Dulling of machine-made pane glass.** ANON. *Glashütte*, **63** [8], 131 (1933).—After a certain time, glass made by the Fourcault method becomes tarnished and has an irridescent surface. To promote melting and to increase the rapidity of drawing (with the result that the glass is badly cooled) the alkali content of the glass is increased too much. M.V.K.

**Reasons for failures of machine-made glass.** A. LEBEDEV. *Keram. i Steklo*, **9** [2], 10–11 (1933).—L. found that streaks in window glass worked on Fourcault machines are due to a varied thickness of the glass sheet which is not caused by an insufficient homogeneity of the glass mass but by uneven cooling of the glass and lack of uniform flow of cold air which cools the glass ribbon at the critical moment of its hardening. M.V.K.

**Modern furnaces for glassmelting.** D. B. GINZBURG AND V. P. SUROVTZEV. *Keram. i Steklo*, **9** [2], 17–19 (1933).—Different types of glassmelting furnaces and their advantages and defects are described. M.V.K.

**Tank furnace with Fourcault canal for 12 machines.** B. F. KUZMICH. *Keram. i Steklo*, **9** [2], 11–16 (1933).—K. discusses the defects of the Fourcault method of producing glass and describes a new shortened tank furnace. M.V.K.

**Depression-proof glass plant depends on careful production methods.** FOSTER-FORBES GLASS CO. *Ceram. Ind.*, **20** [5], 228 (1933).—The production methods used are described. W.W.M.

## Book Review

**Johann Kunckel (1630–1703).** H. MAURACH. Reports from the German Museum. Published by Verein Deutscher Ingenieure, Verlag, G.m.b.H., Berlin, 1933. 34 pp. 3 illustrations and 1 portrait. Price 0.90 Rm. A good deal of the fame of Johann Kunckel is due, perhaps, to his calling as alchemist. Yet K. was an exact scientist even though he started from assumptions which now are known to be erroneous. The German Museum has devoted this booklet to the queer and famous adviser of the glass industry during the 17th Century. The booklet contains a biographical sketch and a section devoted to the products of his labor. K.'s fame was based upon his ruby glass. The value of the ruby glass was rooted in the alchemistic value of gold with which glass is colored. From K.'s time begins the scientific penetration of glassmaking, his chief literary product being "Ars vitraria experimentalis." It was the first book in German containing all knowledge of glassmaking existing up to that time. The booklet makes the reader acquainted with this book, which up into the 19th Century has greatly influenced the making of glass. Kunckel will have a monument in one of the museum halls.

## PATENTS

**Annealing leer.** J. L. DRAKE (Libbey-Owens-Ford Glass Co.). U. S. 1,908,826, May 16, 1933.

**Apparatus for forming sheet or plate glass.** J. L. DRAKE (Libbey-Owens-Ford Glass Co.). U. S. 1,908,825, May 16, 1933.

**Mold for glassware.** LOUIS POGLEIN (McKee Glass Co.). U. S. 1,908,861, May 16, 1933.

**Method and apparatus for feeding glass.** O. M. TUCKER AND W. A. REEVES (Hartford-Empire Co.). U. S. 1,908,936, May 16, 1933.

**Apparatus for feeding molten glass.** K. E. PEILER (Hartford-Empire Co.). U. S. 1,909,152, May 16, 1933, and 1,911,529, May 30, 1933.

**Mold-mounting device.** W. L. MCNAMARA (Capstan Glass Co.). U. S. 1,909,374, May 16, 1933.

**Method and means for making laminated glass.** A. G. WORRALL (Louis J. Kolb). U. S. 1,909,444, May 16, 1933. G. B. WATKINS (Libbey-Owens-Ford Glass Co.). U. S. 1,911,296, May 30, 1933, and 1,913,223, June 6, 1933.

**Method of producing receptacles from molten material.** J. E. MARSDEN (Gayner Glass Works). U. S. 1,909,778, May 16, 1933.

**Glass transfer apparatus.** F. L. CROSBIE (Hazel-Atlas Glass Co.). U. S. 1,909,813, May 16, 1933.

**Glass-polishing apparatus.** W. O. AMSLER (Simplex Engineering Co.). U. S. 1,909,902, May 16, 1933.

**Apparatus for drawing glass.** H. L. HALBACH (Pittsburgh Plate Glass Co.). U. S. 1,909,948, May 23, 1933.

**Process of treating laminated glass.** F. B. TRACE AND R. G. WHITTEMORE (Duplate Corp.). U. S. 1,910,072, May 23, 1933.

**Lens.** E. D. TILLYER (American Optical Corp.). U. S. 1,910,483, May 23, 1933.

**Method and apparatus for fusing lens blanks.** E. M. MORRIS (Bausch & Lomb Optical Co.). U. S. 1,910,708, May 23, 1933.

**Machine and method for processing laminated glass.** G. W. BURK. U. S. 1,910,748, May 23, 1933.

**Drawing nozzle for the manufacture of flashed glass.** BERNHARD ENGELS. U. S. 1,910,759, May 23, 1933.

**Glass-severing mechanism.** K. E. PEILER (Hartford-Empire Co.). U. S. 1,910,856, May 23, 1933.

**Stacker for glassware annealing leers.** ORIE SHACKELFORD (Hartford-Empire Co.). U. S. 1,911,093, May 23, 1933.

**Glassware forming machine.** H. W. INGLE (Hartford-Empire Co.). U. S. 1,911,119, May 23, 1933. O. C. K. HUTCHINSON (Owens-Illinois Glass Co.). U. S. 1,911,998, May 30, 1933.

**Glass-surfacing apparatus.** J. C. BLAIR (Libbey-Owens-Ford Glass Co.). U. S. 1,911,221, May 30, 1933.

**Apparatus for surfacing plate glass.** J. L. DRAKE AND LEROY L. HANDY (Libbey-Owens-Ford Glass Co.). U. S. 1,911,269, May 30, 1933.

**Door for glass tanks.** J. H. RITTER. U. S. 1,911,394, May 30, 1933.

**Process and apparatus for making composite glass sheets.** R. J. A. INGOUF (Blue Ridge Glass Corp.). U. S. 1,911,573, May 30, 1933.

**Corrugated glass light for corrugated roofs and walls.** P. G. MASTERS (Pennsylvania Wire Glass Co.). U. S. 1,911,578, May 30, 1933.

**Method of and means for bedding glass for working.** F. F. SHETTERLY (Blue Ridge Glass Corp.). U. S. 1,911,587, May 30, 1933.

**Ribbon-forming mechanism for glassworking machines.** D. W. STRAIT (Corning Glass Works). U. S. 1,911,591, May 30, 1933.

**Glass-forming machine.** A. M. ALGEO AND G. R. HAUB (Hazel-Atlas Glass Co.). U. S. 1,911,870, May 30, 1933.

**Heat insulator.** GAMES SLAYTER (Owens-Illinois Glass Co.). U. S. 1,912,017, May 30, 1933.

**Machine for forming hollow glass articles.** L. D. SOUBIER (Owens-Illinois Glass Co.). U. S. 1,912,018, May 30, 1933.

**Lighting fixture.** J. H. ALLEN (Inland Glass Works, Inc.). U. S. 1,912,116, May 30, 1933.

**Display device.** J. H. ALLEN (Inland Glass Works, Inc.). U. S. 1,912,117, May 30, 1933.

**Advertising device.** J. H. ALLEN (Inland Glass Works, Inc.). U. S. 1,912,118, May 30, 1933.

**Lamp shade.** J. H. ALLEN (Inland Glass Works, Inc.). U. S. 1,912,119 and 1,912,120, May 30, 1933.

**Means for circulating glass in the forehearths of glassmelting tanks.** C. H. RANKIN (Rankin Automatic Glass Feeder Co.). U. S. 1,912,306, May 30, 1933.

**Glassworking machine.** V. L. RONCI (Bell Telephone Laboratories, Inc.). U. S. 1,912,405, June 6, 1933.

**Leer loader.** R. D. STURM (Hazel-Atlas Glass Co.). U. S. 1,912,503, June 6, 1933.

**Nonshattering glass and method of making.** IWAN OSTROMISLENSKY (Naugatuck Chemical Co.). U. S. 1,913,127, June 6, 1933.

**Heat control for working end of tanks.** W. T. BARKER, JR. (Hartford-Empire Co.). U. S. 1,913,302, June 6, 1933.

**Method and apparatus for supplying glass.** VERGIL MULHOLLAND (Hartford-Empire Co.). U. S. 1,913,311, June 6, 1933.

**Securing metal supports to fused silica articles.** LEROY JAMES BUTTOLPH (British Thomson-Houston Co., Ltd.). Brit. 364,188, Oct. 7, 1929. A method and machine are described for attaching a metal ring, ferrule, or annular support to hollow articles of fused quartz, especially the envelope of a Hg-vapor lamp, involving heating till the $SiO_2$ is plastic. (*C.A.*)

**Manufacture of splinterless glass.** J. W. C. CRAWFORD, J. S. B. FLEMING, AND IMPERIAL CHEMICAL INDUSTRIES, LTD. Brit. 391,114, May 3, 1933.

**Apparatus for the production of wired glass.** J. GASKELL. Brit. 391,297, May 3, 1933.

**Bullet-proof composite glass.** A. KAMPFER AND A. C. PLOTZE. Brit. 391,356, May 3, 1933.

**Manufacture of glass tubes.** L. SANCHEZ-VELLO. Brit. 391,391, May 3, 1933.

**Grinding and polishing lenses.** J. DESENBERG. Brit. 391,470, May 10, 1933.

**Manufacture of hollow glassware.** L. MELLERSH-JACKSON (Hartford-Empire Co.). Brit. 391,558, May 10, 1933.

**Glass tile and process of manufacture.** W. A. PREYER. Brit. 392,121, May 17, 1933.

**Glass bottle making.** E. A. HAILWOOD. Brit. 392,285, May 24, 1933.

**Method and means for packing glassware.** UNITED GLASS BOTTLE MFRS., LTD., JOHNSEN & JORGENSEN FLINT GLASS, LTD., AND H. J. JUDD. Brit. 392,331, May 24, 1933.

**Mold for blowing glassware.** SOC. ANON. D'ÉTUDES ET DE CONSTRUCTIONS D'APPAREILS MÉCANIQUES POUR LA VERRERIE. Brit. 392,443, May 24, 1933.

**Glass.** SOC. ANON. D'ÉTUDES ET DE CONSTRUCTIONS D'APPAREILS MÉCANIQUES POUR LA VERRERIE. Fr. 41,254, July 1, 1931. Means for continuously feeding glass from the furnace is described. See also *Ceram. Abs.*, **11** [7], 411 (1932). (*C.A.*)

**Tempering glass.** SOC. ANON. DES MANUFACTURES DES GLACES ET PRODUITS CHIMIQUES DE SAINT-GOBAIN, CHAUNY ET CIREY. Fr. 686,890, March 13, 1929. Sheets of glass are tempered by heating them, suspended vertically, to a uniform temperature corresponding with that at which softening begins to take place, and submitting them to violent jets of air striking the two faces normally until completely cold. *Ibid.* 41,362, July 24, 1931. Improved means for directing the air onto the glass and for suspending the glass are described. (*C.A.*)

**Apparatus for determining or controlling the temperature of molten glass.** UNITED GLASS BOTTLE MANUFACTURERS, LTD. Fr. 739,521, July 6, 1932. (*C.A.*)

**Glass.** SOC. ANON. DES MANUFACTURES DES GLACES ET PRODUITS CHIMIQUES DE SAINT-GOBAIN, CHAUNY ET CIREY. Fr. 740,747, Oct. 30, 1931. Means are specified for flowing the molten glass onto a table. (*C.A.*)

**Glass crucible.** SIMPLEX ENGINEERING CO. Fr. 741,020, Aug. 10, 1932. The construction of a crucible for fusing and refining glass is described. (*C.A.*)

**Frosting glass.** ELISABETH HONIGMANN (Patent-Treuhand-Ges. für elektrische Glühlampen m.b.H.). Ger. 565,914, Nov. 12, 1931. $B_2O_3$ glass is frosted by a bath of HF to which $H_3BO_3$, $HBF_4$, or their salts are added. See also *Ceram. Abs.*, **12** [6], 224 (1933). (*C.A.*)

**Clouded glass.** FRANZ SALAQUARDA (Walter Schröder). Ger. 566,620, Aug. 1, 1930. Clouded glass contains more than 35% PbO, no $B_2O_3$, and the usual mixture of $SiO_2$, alkali, alkaline earth, and P and F compounds. The example describes glass containing PbO 48, $Ce_2O_3$ and $ZrO_2$ 1.5, $R_2O$ 7.5, $SiO_2$ 39, $AlF_3$ 3, and $Ca_3(PO_4)_2$ 1%. (*C.A.*)

**Rolling or kneading quartz glass free from streaks.** ARTHUR KRÖNER (W. C. Heraeus G.m.b.H.). Ger. 567,863, Nov. 29, 1931. (*C.A.*)

**Devitrified glass articles.** CARL TRENZEN. Ger. 569,310, Jan. 3, 1931. Ordinary Ca-Na glass is fused at about 1380° with 10 to 45% of a slag consisting mainly of pseudowollastonite, and the melt is molded as usual. Crystallization is complete by the time the article is sufficiently cool to be removed from the mold. A suitable slag has the composition $SiO_2$ 45.4, $Al_2O_3$ 5.6, $Fe_2O_3$ 0.6, CaO 47.8, and P 0.6% and is obtainable as a by-product in the manufacture of P from phosphorites. (*C.A.*)

**Devitrifying metallurgical slags, glass melts, etc.** FELIX SINGER. Ger. 570,148, Oct. 18, 1929. A plurality of known crystallizing agents is added to the melt, the agents selected being elements of different periodic groups or compounds of such elements. (*C.A.*)

**Preventing blurring of glass.** S. S. GROMOV. Russ. 27,444, July 11, 1931. Blurring of glass is prevented by a simultaneous application to its surface of a solution of glue in warm water containing pure alcohol together with small amounts of water glass and a solution of formalin in alcohol. See also *Ceram. Abs.*, **12** [3], 105 (1933). (*C.A.*)

## Structural Clay Products

**Results of tests on seven demonstration structures with summary covering tests on twenty structures.** E. E. KRAUSS, JUDSON VOGDES, AND J. R. SHANK. *Bull. Amer. Ceram. Soc.*, **12** [6], 166–97 (1933).

**Rostone—a new building material with a shale base.** H. C. PEFFER, RICHARD L. HARRISON, AND R. NORRIS SHREVE. *Brick Clay Rec.*, **82** [5], 175–76 (1933).—Shales having the approximate analysis of alumino-disilicic acid are ground to a fineness of 90% through a 325-mesh sieve in the dry state, and the material is thoroughly incorporated with thoroughly slaked calcium hydrate in proportions which vary with the different aluminosilicates, pressed at 2500 lb./sq. in., allowed to stand at room temperature conditions in the open air for several hours, and autoclaved by means of saturated steam at low pressure, after which it is allowed to cool. The resultant product, Rostone, as normally produced shows a compressive strength of 6000 to 8000 lb./sq. in. The material is quite resistant to dilute acids and to boiling sodium carbonate solutions. See also abstract by Peffer, *Ceram. Abs.*, **11** [4], 244; [12], 616 (1932). E.J.V.

**Manufacturing sewer pipe with de-aired clay.** CHESTER R. AUSTIN. *Brick Clay Rec.*, **82** [5], 173 (1933); reprinted from O. S. U. Eng. Expt. Sta. *News*, **5** [2], 3 (1933).—A series of tests run on sewer pipe made with a de-aired solid clay slug showed that the body properties were improved, affording better body structure, lower absorption, lower apparent porosity, fewer small blisters on the exterior surface, great reduction in the number of large blisters, and higher crushing and transverse strengths, though the slugs did not knit properly. The use of butane for de-airing has only a minor effect in increasing desirable properties. E.J.V.

**Data. XVI.** T. W. GARVE. *Clay-Worker*, **99** [5], 180–81 (1933).—G. continues with a presentation of data on flue lining, hollow wall tile of both end and side construction, partition tile, furring tile, and the various sorts of roofing tile. Sizes and weights are given. For Part XV see *Ceram. Abs.*, **12** [7], 265 (1933). E.J.V.

**Efflorescences in brick. I.** ALIX CORNILLE. *Rev. mat. constr. trav. pub.*, No. 283, pp. 65–67*B* (1933).—The use of baryta and chloride to prevent efflorescence is discussed. M.V.K.

**Lime in brick clays.** ANON. *Tonind.-Ztg.*, **57** [31–32], 367–68 (1933).—The lime may be removed by washing or by special machines. In most cases fine grinding of the lime-containing clay will result in improving the quality of the products. By firing the clay at a high temperature the lime may be made harmless. W.M.C.

**Time of freezing in testing building materials.** E. ERLINGER AND H. KOSTRON. *Tonind.-Ztg.*, **57** [34], 389–91 (1933).—German standard specifications provide that freezing tests should be carried out for at least 4 hr., the temperature being −4 and −15°C, respectively. Experiments were carried out by inserting a thermocouple into the brick and studying its behavior during the entire cooling cycle. A number of graphs shows that freezing tests should be extended over more than 4 hr. A loose packing of the brick will give better results than a tight packing. W.M.C.

**Hard-fired brick for road construction.** A. HIELSCHER. *Tonind.-Ztg.*, **57** [39], 452–53 (1933).—Large-scale construction of roads is being planned by the new German government. The need of hard-fired brick of an excellent quality is emphasized, and the standardization of these brick is proposed. See also *Ceram. Abs.*, **12** [6], 225 (1933). W.M.C.

**Need of research in the building industry.** A. HOFHERR. *Tonind.-Ztg.*, **57** [39], 447–49 (1933).—A department for carrying out research for the building industry has been incorporated into the University of Marburg, Germany. Research is proposed for the following problems: (1) strength of brick and tile columns, (2) decrease of thickness of walls for buildings, (3) improvements in mortars for the joints, (4) preven-

tion of the passage of moisture into the building, (5) heat and noise insulation materials, (6) types of ceilings, and (7) testing of roofing tile and all other parts of the roof. W.M.C.

**Use of common brick for the construction of silos.** W. GRESSLER. *Tonind.-Ztg.*, **57** [36], 416–17 (1933); see also *Ceram. Abs.*, **12** [7], 265 (1933). W.M.C.

**Originality in brick and brickmaking.** A. ZAIMAN. *Brit. Clayworker*, **42** [492], 20–24 (1933).—Z. gives a historical sketch of the brickmaking industry and discusses the four common methods of brick manufacture. The de-airing of clays, addition of common acids to pugging water, manufacture of lightweight brick, and driers, kilns, and general mechanization are briefly reviewed. General brick forms, such as cellular flettons, perforated brick, and hollow blocks, and their colors and textures are also discussed. R.A.H.

PATENTS

**Process of producing cellular building material.** KEMPER SLIDELL AND S. Q. LEE (American Face Brick Research Corp.). U. S. 18,844, May 30, 1933 (reissue).

**Guide for bricklayers' use.** H. A. GOLT. U. S. 1,909,267, May 16, 1933.

**System of soft-mud brick manufacture and mold therefor.** J. A. CROWELL (J. B. Crowell & Son). U. S. 1,909,523, May 16, 1933.

**Brick veneer construction.** F. H. MEIER. U. S. 1,909,625, May 16, 1933.

**Brickmaking.** R. E. PARRY (Dennis F. O'Connell). U. S. 1,910,496, May 23, 1933.

**Flashing block, brick, or tile.** H. L. HANSBERRY (John M. Crowe). U. S. 1,910,605, May 23, 1933.

**Method of producing clay products.** PATTILLO HIGGINS. U. S. 1,912,772, June 6, 1933. The method of producing a clay product consists in mixing two clays having high and low melting points, respectively, subjecting the mixture to sufficient heat to fuse only one of the clays, and maintaining the temperature to cause the fused clay to coalesce with the other clay.

**Building brick.** H. TOMLINS. Brit. 391,580, May 10, 1933.

**Manufacture of brick.** F. T. MEEHAN AND F. M. LEA. Brit. 392,198, May 24, 1933.

**Light, porous, strong building material from clay.** A. N. P. BOUTON. Belg. 390,566, Sept. 30, 1932. Most of the fuel required for burning is introduced into and uniformly distributed throughout the plastic mass before molding. (*C.A.*)

**Brick.** RAOUL ROUX, PAUL GUÉRY, AND PHILIPPE WEYERS. Fr. 41,404, Jan. 25, 1932; addition to 710,803. Silicates of Mg and double silicates of Mg and Ca are incorporated with cellulose and clay in a composition for making brick. (*C.A.*)

**Device for blowing granular materials into a ceramic firing kiln.** ARNO ANDREAS. Ger. 566,573, June 17, 1930. (*C.A.*)

## Refractories

**Selecting the right chrome ore.** A. DE MACEDO. *Blast Fur. Steel Plant*, **21** [5], 279–80 (1933).—The development of more precise ways of selecting the right chrome ore has resulted in improved quality of chrome refractories. Formerly, chrome ores were selected on the basis of chromic oxide and silica content, but it has been shown that ores with proper analyses did not always have the same adaptability for refractory purposes. Some shattered and spalled badly in the basic open hearth while others had poor staying qualities when used to daub panels or protect walls. A simple test for staying qualities is described. E.J.V.

**Silica as a refractory material. II.** C. N. WITHEROW. *Brick Clay Rec.*, **82** [5], 164–65 (1933).—W. shows that silica is polymorphous and classifies its several inversions under rapid and sluggish inversions. A list of the various inversions is given and their properties are discussed. The occurrence and properties of silica, tridymite and cristobalite, and fused silica are next taken up with a number of the other silicate minerals which are important in a limited way as refractory materials. For Part I see *Ceram. Abs.*, **12** [7], 266 (1933). E.J.V.

**Armstrong's EF brick.** ARMSTRONG CORK & INSULATION CO. *Blast Fur. Steel Plant*, **21** [5], 272–73 (1933).—As no firebrick protection is necessary with the EF brick, it combines the service secured from fire brick and the fuel saving obtained from insulating brick. It can not be used where it will be exposed to abrasion or slagging action. A 9-in. wall of EF brick has the same heat loss as a $22^1/_2$-in. fire brick and $2^1/_2$-in. ordinary insulating brick wall. A cubic foot of EF brick laid up and faced with

sillimanite or mullite cement weighs about 60 lb. compared to 150 lb. for fire brick on the same basis. Methods of laying these brick for different types of furnaces are described. E.J.V.

**Some uses of refractory materials in the foundry: blacking and plumbagoes.** J. G. A. SKERL. *Refrac. Jour.*, **9** [3], 91–94 (1933).—S. discusses the use of refractory material for facing the surface of foundry molds. Heat-resisting properties of the various forms of carbon are given. Graphite (plumbago) is the best form for facing molds because of its high ignition temperature. S. writes on the use of binders with the graphite and discusses specifications of blackings and graphites. Molding sands, their bonds, and characteristics of mills used in their preparation are also covered. See also *Ceram. Abs.*, **12** [6], 230 (1933). W.W.M.

**Manufacture of crucibles stable to slag from magnesia and alumina.** HERMANN SALMANG AND NICOLAUS PLANZ. *Feuerfest*, **9** [3], 46 (1933); for abstract see *Ceram. Abs.*, **12** [6], 229 (1933). M.V.K.

**Graphite for crucibles.** WERNER FRÖHLICH. *Chem.-Ztg.*, **56**, 809–10 (1932).—A general account is given of native graphite, its occurrence, preparation, properties, and uses. The advance of Madagascar graphite in comparison with that of Ceylon is due to its uniformity and lack of artificial "blending" by the producers. American graphite is dismissed as of inferior grade and that of Germany is said to be but little better; mixtures of Ceylon and Bavarian graphite give excellent crucibles. A good graphite crucible holds up well at 1800° (a fireclay crucible softens at that temperature) until the C has been fired out, conducts heat better, and is not as much affected by fluxes as a clay crucible. (*C.A.*)

**Economic regenerators for open-hearth furnaces.** H. TRINIUS. *Iron Coal Trades Rev.*, **126** [3403], 790 (1933).—T. recommends separate gas and air chambers strongly braced and built with porous type brick and with the walls treated with a coating to render them gas tight. For the checkers, brick of square section, preferably 2 x 2 in., are found to be economical in spite of higher first cost. The brick must be easily transported, easily laid, and able to withstand high temperatures and wide fluctuations of temperature. In the case of basic furnaces the thickness of the brick must be increased in the upper part of the checker where highest temperatures prevail because the silica brick used are more susceptible to slag attack than fire brick and flux in course of time. If it is necessary to employ more silica than is normally required in the upper courses of a checker, a margin of safety must be allowed to ensure that the lowest temperature of the silica brick does not fall below the critical point (575°C). W.E.R.

**Carbon brick for electric kilns.** C. KUHLMANN. *Stahl Eisen*, **53** [12], 306 (1933).—Carbon brick are being used as a lining for electric melting furnaces. No other refractory material will withstand the heavy chemical and physical attack in this type of furnace. As a rule the furnace is lined with a mixture containing calcined carbon of different grades such as anthracite, coke, and electrode residues. Cracks will occur in firing the lining. Separate layers and places of a high porosity will often form. The use of fired carbon brick as a furnace lining is emphasized. These brick should be laid with very small joints. Prefired carbon brick will show a small thermal expansion and a good resistance to thermal shock. Illustrated. W.M.C.

**Use of dolomite.** W. MORIZ. *Tonind.-Ztg.*, **57** [34], 393–95 (1933).—Dolomite is being used for the construction of houses and for paving roads. Dolomite refractories are found in blast furnaces, cement kilns, and open-hearth furnaces. Methods of inserting dolomite linings in kilns are discussed. Unfired brick have been used for this purpose in recent years. Dolomite is also being used as a basic material in the manufacture of soda and other chemical products. W.M.C.

**Refractories and kiln construction.** J. C. MILBORN. *Arch. Suikerind.*, **40**, 490–91 (1932).—Quartz schist is suitable for lining lime kilns. See following abstract. (*C.A.*)

**Refractories and kiln construction.** W. G. LINGBEEK. *Arch. Suikerind.*, **39**, 1108–16, 1117–32, 1133–43 (1931).—The physical chemistry of refractories is reviewed and the practical application to construction of lime kilns is discussed. For Java conditions it is best to use a very hard chamotte of low porosity with 30 to 35% $Al_2O_3$ and with a refractory value corresponding to Seger cones 31 to 32. The kiln must be constructed and operated in such a way that overheating is avoided as much as possible. The kiln may be cooled efficiently by building a water-tube boiler as a jacket around it; the steam thus generated may be utilized in various ways. (*C.A.*)

**One ton crucible melting plant.** ANON. *Metal Ind.* [London], **42** [16], 429–30 (1933).—A new 1-ton oil-fired crucible furnace is described in detail. M.V.K.

**Metallurgy and uses of zinc.** STANLEY ROBSON. *Metal Ind.* [London], **42** [14], 369–72; [15], 397–400; [16], 421–24 (1933).—Zinc production and furnaces utilized and refractories used in modern zinc furnaces are reviewed. M.V.K.

**Furnace design.** S. N. BRAYSHAW. Presented at Manchester Assn. of Engineers Meeting, March 10, 1933; abstracted in *Refrac. Jour.*, **9** [4], 172 (1933); for abstract see *Ceram. Abs.*, **12** [7], 267 (1933). W.W.M.

**Possible applications of siemensite in the chemical industry.** J. SCHMAUSER. *Chem. Fabrik*, **6**, 119–22 (1933).—Siemensite ($Cr_2O_3$ 20 to 40, MgO 18 to 30, $Al_2O_3$ 25 to 40, residual matter 8 to 14%) can be cast from a melt to form good blocks. See also *Ceram. Abs.*, **12** [5], 194 (1933). (*B.C.A.*)

**Refractory coatings.** GALLUS. *Eng. Boiler House Rev.*, **46** [7], 464 (1933); for abstract see *Ceram. Abs.*, **12** [5], 193 (1933). W.E.R.

**Magnesite refractories.** P. P. BUDNIKOFF AND Z. YA. TABAKOV. *Domez*, No. 9, pp. 24–31 (1932).—A review is presented. (*C.A.*)

**Refractories in the metallurgical industry.** A. T. GREEN. *Refrac. Jour.*, **9** [3], 97–98 (1933); for abstract see *Ceram. Abs.*, **12** [7], 266 (1933). W.W.M.

**Refractory fireclay ware produced by the method of dry pressing at the Chassov-Yar plant "Ukrogneupor."** P. P. BUDNIKOFF. *Domez*, No. 12, pp. 58–60 (1932).—Refractory brick, crucibles, and large blocks were prepared by the dry-press method. (*C.A.*)

**Elastic distortion and plastic deformation of refractory brick at 20°C and at higher temperatures.** K. ENDELL AND W. MÜLLENSEIFEN. *Ber. deut. keram. Ges.*, **14** [1], 16–28 (1933).—A new device for the determination of elastic and plastic distortion of refractory brick at room temperatures is described. The results obtained on ten different refractory brick with this apparatus make it possible to detect a new relation between torsion stresses and the specific distortion in the elastic and plastic range. A relation between the modulus of elasticity and resistance to compression is set up for ceramic materials, slags or clinker, and glasses. The sphere of refractory brick is divided into three groups with increasing modulus of elasticity and resistance to compression. The following causes, which may be active separately or in combination, for high distortion of certain refractory brick have been detected: (1) grain size combination, grain bond, type of bonding medium; (2) smooth crystallographic rearrangement ($SiO_2$); (3) cleavage planes in crystals, *e.g.*, periclase. Reference is made to the significance of these characteristics on the elastic and plastic deformability and resistance to temperature changes of refractory brick. Curves for softening under tension of different refractory brick up to 1500° were determined in a torsion apparatus in which heat could be applied to the specimen under test. Illustrated. E.J.V.

**Testing of refractories under load.** HERMANN BITTNER. *Chem. Eng. Mining Rev.*, **24**, 303–306 (1932). (*C.A.*)

**Refractory clays of northern Ontario.** W. S. DYER AND A. R. CROZIER. *Can. Mining Met. Bull.*, No. 254, pp. 238–52 (1933).—Refractory clay of Lower Cretaceous age occurs on four rivers of the James Bay watershed. Descriptions of the deposits and summaries of tests on the clays are given. See also *Ceram. Abs.*, **11** [11], 590 (1932). G.M.H.

**Canadian electric furnace industry.** ALFRED STANSFIELD. *Trans. Electrochem. Soc.* (preprint), **63**, 15 pp. (1933).—The economic development of large amounts of hydroelectric power in many parts of Canada has led to an important growth of industries producing Al, $CaC_2$, artificial abrasives, ferro-alloys, and other electric furnace products. These industries are described and their value to Canada and the U. S. is indicated. (*C.A.*)

**Measurement of metal temperature on heat-receiving side of heat-exchanging apparatus.** A. WILLIAMS. *Amer. Soc. Mech. Eng. Preprint*, No. 53, 5 pp. (Dec., 1932). *Bull. Brit. Non-Ferrous Metals Research Assn.*, Serial No. 11, 797.—Modern design of heat-transfer apparatus frequently involves use of very high metal temperatures. In measuring temperature of metal walls under operating conditions, thermocouple wires are attached to outside walls. The wires pass through a high-temperature zone, as in the case of hot flue gases, and are heated above the temperature of the wall. This heat flows through the wires to the junction. To determine the magnitude of this error, tests were made under severe operating conditions. (*B.B.N.F.M.R.A.*)

PATENTS

**High-pressure process of molding refractory brick.** R. P. HEUER. U. S. 1,911,152, May 23, 1933.

**Metal-coated refractory material and process of making.** H. H. HARRIS. U. S. 1,911,189, May 30, 1933.

**Tuyère block.** ARTHUR WATHEY. U. S. 1,911,862, May 30, 1933.

**Basic refractory brick, etc.** C. S. GARNETT. U. S. 1,912,894, June 6, 1933. An intermediate product is composed of a mixture of oil with an agglomerable material consisting of burned dolomite in which the lime is in combined form.

**Furnace wall.** OSCAR NYGAARD. U. S. 1,912,912, June 6, 1933.

**Suspended refractory structures.** L. S. LONGENECKER. U. S. 1,913,168, June 6, 1933.

**Manufacture of refractory substances.** T. R. HAGLUND. Brit. 391,662, May 10, 1933.

**Refractory brick.** R. P. HEUER. Brit. 391,858, May 17, 1933.

**Cast refractory articles and methods of making.** R. HADDAN (Corning Glass Works). Brit. 392,364, May 24, 1933.

**Refractory materials.** VEREINIGTE STAHLWERKE A.-G. Fr. 740,467, July 25, 1932. The decomposition of gases such as CO, $CH_4$, or its homologs by contact with refractory materials containing oxide of Fe is prevented by treating the materials with boric acid, its inorganic or organic salts, alkali salts, Pb, Ni, Cr, Mg, Hg, Mn, Al, As, Zn, Cd or their oxides or compounds, or alkali or $NH_4$ phosphates. (*C.A.*)

**Refractory material.** TURE R. HAGLUND. Fr. 740,668, Aug. 2, 1932. A refractory material containing, after solidification, at least 50% by weight of crystals of spinel from MgO is obtained by fusing a mixture containing, besides spinels, at least 8% of compounds more easily fusible than the latter, such as silicates, titanates, or aluminates, the content of which in oxides of Mg and Ca is either a very small proportion or more than 45%. (*C.A.*)

**Refractory materials.** DWIGHT & LLOYD METALLURGICAL CO. Fr. 740,798, July 19, 1932. A refractory material is made by intimately mixing one or more substances of the nature of dolomite, magnesite, limestone, etc., and a suitable proportion of a fuel, lighting the fuel on one of the surfaces of a thin layer of the mixture, and passing air through so that an intense heat is produced. The material is fused and produces a cellular mass. (*C.A.*)

**Refractory articles.** CHAMOTTEFABRIK THONBERG, A.-G. Ger. 570,461, March 6, 1929. Refractory articles are made by molding and firing a mixture of chamotte with about 8% of feldspar or dolomite and about 2% of an organic binder comprising sulfite cellulose waste lye or molasses. (*C.A.*)

**Refractories.** F. I. KANDUIKIN. Russ. 27,326, Aug. 10, 1931. The required mechanical strength is given to refractory goods by mixing quartz sand with about 30% tripoli low in Fe and containing about 10% $H_2O$. The ingredients are properly mixed, formed, and fired at a temperature sufficient for the conversion of the crystalline quartz. (*C.A.*)

## Terra Cotta

**Manufacture and firing of enameled products (brick and sanitary products).** ALBERT GRANGER. *Céram. Verrerie*, pp. 473–74 (1932). (*C.A.*)

**Firing stoneware products.** J. GREWE. *Tonind.-Ztg.*, **57** [35], 403 (1933).—G. suggests firing partly under reducing and partly under oxidizing conditions. This is claimed to be more economical than firing in a reducing atmosphere alone. W.M.C.

**Manufacture of terra cotta pipe.** A. L. *Corriere Ceram.*, **14** [2], 49–53 (1933).—The mining, weathering, preparation, grinding, and mixing of the clay, and shaping, drying, and firing are discussed in regard to obtaining a more economic production of terra cotta pipe. M.V.K.

**Manufacture of flowerpots by machinery.** ANON. *Brit. Clayworker*, **42** [492], 18–19 (1933). R.A.H.

### PATENTS

**Earthenware and stoneware tubes, pipes, gullies, etc.** G. L. WATKINS. Brit. 391,181, May 3, 1933.

**Roofing tile.** J. BOARD & CO., LTD., AND W. S. AKERMAN. Brit. 391,389, May 3, 1933.

**Glazing.** SCHÜTTE A.-G. FÜR TONINDUSTRIE AND THEODOR SCHUMANN. Ger. 566,827, Feb. 25, 1931. A glaze corresponding to "terra sigillata" is produced on earthenware by soaking in $H_3BO_3$ or dusting with B compounds, heating to 600 to 1050° in a reducing atmosphere, and finally firing. (*C.A.*)

**Earthenware.** HANS BONTE. Ger. 567,532, Nov. 22, 1929. The formation of salt glaze on earthenware is prevented by using materials with a high $Al_2O_3$ or MgO content. (*C.A.*)

## White Wares

**Dielectric strength of porcelain: the influence of porosity.** A. J. MONACK AND R. K. SMITH. *Jour. Amer. Ceram. Soc.*, **16** [7], 293–95 (1933).

**Rapid firing of semiporcelain.** J. T. ROBSON. *Jour. Amer. Ceram. Soc.*, **16** [7], 296–98 (1933).

**Potash-soda-lime feldspar eutectic study.** J. A. MARTZ. *Jour. Amer. Ceram. Soc.*, **16** [7], 299–304 (1933).

**Electrical conductivity of commercial dielectrics and its variation with temperature.** J. D. CLARK AND J. W. WILLIAMS. *Jour. Phys. Chem.*, **37** [1], 119–31 (1933).—Determinations were made of the specific volume conductivities of ten "amorphous" substances as a function of temperature. Possible mechanisms of the conduction process are briefly discussed. G.R.S.

**Refractory porcelain bodies.** HIGGINS AND MONTGOMERY. Toronto Univ. Eng. *Bull.*, pp. 158–71 (1932); *Refrac. Jour.*, **9** [4], 172 (1933).—A general account is given of electrical refractory porcelain compositions. Bodies consisting of alumina, silica, and magnesia were tested, more particularly from the point of view of studying the influence of the magnesia content on the physical properties, including porosity, absorption, shrinkage, heat resistance, and electrical conductivity. The compositions now in industrial use are criticized. W.W.M.

**Utilization of pyrophyllite in porcelain and faience.** L. V. OMININ AND V. T. POPOVA. *Keram. i Steklo*, **9** [2], 20–23 (1933).—Two kinds of pyrophyllite ($Al_2O_3 \cdot 4SiO_2$) were used, plastic, similar to clay, and a pink. The results are as follows: (1) Pyrophyllite lowers the plasticity of the mass. (2) It considerably reduces shrinkage on firing which is a decided advantage over kaolin. (3) It does not change the mechanical strength of the mass. (4) It does not change the coefficient of linear expansion or diminish the thermal stability of fully vitrified bodies. In bodies with a 6 to 8% porosity, it increases the coefficient of linear expansion and lowers the thermal stability. (5) It does not change the external color of the body. (6) It considerably lowers the translucency of the body. See also article by Tailby, *Ceram. Abs.*, **12** [4], 163 (1933). M.V.K.

**Scientific and practical study of principal products for flooring in dwellings. III.** F. CHALAMEL. *Rev. mat. constr. trav. pub.*, No. 283, pp. 68–71*B* (1933).—C. discusses the scientific determination of the chemical resistance of products utilized. For Part II see *Ceram. Abs.*, **12** [7], 270 (1933). M.V.K.

**Pour spots on ceramic ware. II.** ANGELO CASTIGLIONI. *Industria chimica*, **8**, 14–16 (1933).—Spots are produced by argillaceous suspensions particularly rich in colloids. These colloids acting as fluxes may cause a vitreous spot which prevents the proper absorption of glaze. For Part I see *Ceram. Abs.*, **11** [12], 623 (1932). (*C.A.*)

**Newly designed tile keeps pace with modern architecture.** AMERICAN ENCAUSTIC TILING CO. *Ceram. Ind.*, **20** [5], 242 (1933).—The reasons for the modeled shape for tile are (1) to attain a single long unit effect, (2) to provide variation in shades and colors, and (3) to accentuate high-lights and shadows, giving greater brilliancy in contrast. W.W.M.

**Shaping porcelain plates in pairs.** L. YA. BENDET. *Keram. i Steklo*, **9** [2], 8–10 (1933).—B. describes a new apparatus used for shaping porcelain plates in pairs. The advantages of using this device are enumerated. M.V.K.

### Book Review

**Behavior of Ceramic Materials against Tension and Compression.** FRITZ HEUMANN. Published by Verein Deutscher Ingenieure, Berlin, 1933. 42 pp. 40 illustrations and 4 tables. 4.50 Rm. The cause of the loss in the manufacture of porcelain insulators has been argued for about 20 years, and the problem of fatigue has been rejected by the porcelain industry. The electric industry blames partly the porcelain and partly the joint for the failure. The presented evidence was merely based upon observation. The resistance of pure porcelain is investigated. It is the first systematic investigation of the behavior of ceramic materials subjected to permanent strains along the lines of fatigue similar to metals. The tests were made on 10 different compositions whereby some duration tests were extended to approach the ultimate strength

up to $1 \times 10^7$ load variation. The values of duration strength were placed in relation to the values of static strength. The extension of vibration cracks, the notch effect, and the influence of the glaze were determined. Extensive measurements revealed that far below the ultimate loading a change in the inner capacity for work (perhaps simply "resistance" (note of translator)) exists pointing to a change in structure. The results are of commercial importance to the electric as well as to the porcelain industry. They also prove that porcelain, similar to metals, shows fatigue. An essential difference, however, is presented here in that the strength is but little decreased by duration strain. In any event, the fatigue of the porcelain body can not be made responsible for the production losses of insulators. An inspection of the static values alone is sufficient. It is important for scientific material testing and applied physics to know that such brittle materials in principle do not behave differently from metals. The mensuration of inflection will also be of interest, especially its change owing to the duration strain, its numerical valuation, and the influence of intervals of repose.

#### PATENTS

**Concealed lavatory.** W. H. HENDRICKSON (Abingdon Engineering Corp.). U. S. 1,909,618, May 16, 1933.

**Ceramic materials and method of making.** T. G. MCDOUGAL (A C Spark Plug Co.). U. S. 1,909,785, May 16, 1933. An aluminum silicate for use in the manufacture of ceramic ware has a higher alumina to silica ratio than kaolin, can be combined with a flux, and is in an unstable crystalline form.

**Package for china.** VAUGHAN WEIDEL. U. S. 1,908,940, May 16, 1933.

**Glazed tile, pottery, etc.** W. AND B. MAGUIRE. Brit. 391,646, May 10, 1933.

**Coloring porcelain.** HERMANN EISENLOHR (Deutsche Gold- und Silber-Scheideanstalt vorm. Roessler). Ger. 566,757, June 9, 1931. A yellow pigment for applying to hard-fired porcelain before glazing consists of 1 part of $UO_2$ and more than 10 parts of $ZrO_2$ heated to 1700 to 1900°. (*C.A.*)

**Machine for glazing shallow chinaware.** I. I. GRINBERG. Russ. 27,873, April 10, 1931. (*C.A.*)

## Equipment and Apparatus

**Measurement of the absorption and retention of gases and vapors by solids.** B. MOORE. *Jour. Soc. Chem. Ind.*, **52** [12], 76–78 (1933).—A description is given of an apparatus which was designed to measure in a simple, accurate manner (1) the absorption of gases and vapors by solids at pressures not exceeding atmospheric, and (2) the retention of gases by solids. G.R.S.

**Measurement of large volumes of gas.** ANON. *Metallurgia*, **8** [43], 27 (1933).—A new curved tube manometer is described. M.V.K.

**Viscosity as a material constant and its measurement.** K. FISCHER. *Chem. Fabrik*, pp. 446–50, 459–61, 471–73 (1932).—The relation between viscosity and other material constants and the dependence of viscosity on various conditions are discussed with 27 references. The construction of several types of apparatus is shown. A table shows the basic principles, accuracy, constants, temperature limits, substances to which adapted, time for a determination, minimum amount of substance required, and price for 15 viscometers. (*C.A.*)

**Use of a refractometer with variable refracting angle.** R. D. MCLELLAN. *Amer. Mineralogist*, **18** [4], 138–47 (1933). G.R.S.

**Care of pyrometers used in the clay industry.** R. C. KENNAN. *Clay-Worker*, **99** [5], 178–79 (1933); *Brick Clay Rec.*, **82** [5], 174–75 (1933).—After a brief explanation of a simple thermoelectric pyrometer system in which the three fundamental parts, thermocouples, lead wires, and instrument, are pointed out, K. gives a detailed explanation of the care necessary for each of these parts. The carrying of spare parts and a periodic check-up by a service man are also recommended. Illustrated. E.J.V.

**Simple universal camera for X-ray and crystal structure analysis.** E. SAUTER. *Z. Krist.*, **85** [1–2], 156–59 (1933).—Its construction is illustrated with diagrams. Three kinds of X-ray photographs can be made with the camera. G.R.S.

**Pulverizing machines.** M. IGEL. *Tonind.-Ztg.*, **57** [37], 426–28 (1933).—Several types of modern crushers are discussed. Illustrated. W.M.C.

**Grinding economies to save 25% in power cost of Portland cement.** NATHAN C. ROCKWOOD. *Rock Prod.*, **36** [4], 42–44 (1933).—R. states that 77% of the total power requirement for Portland cement manufacture is expended in grinding operations.

A new type of pulverizer is described which saves 30% of this power. Tabulated and graphic data are given for tests made on grinding raw material and clinker in this mill. Grindability factors are given for a number of materials. W.W.M.

**Use of a composite grinding load in tube milling on the Witwatersrand.** F. WARTENWEILER. *Jour. Chem., Met., Mining Soc. S. Africa*, **32**, 262–82 (1932).—By using a mixture of steel balls and ore pebbles (about 1:2) as the grinding medium in tube mills in 3 plants, capacities were increased (15% in 1 plant) over those for straight pebble-mill grinding. A shortage of suitable pebbles made the step necessary. In one plant a more selective grinding and an increase in extraction resulted. Operations at these 3 plants are described and detailed data presented. Liner life is increased about 7% when the composite load is used. Cyanide consumption has not been increased by the Fe. Power consumption is increased 15 to 17%. Milling costs are given and show no over-all rise by the use of a composite load. (*C.A.*)

**Application of Andreasen's sedimentation apparatus in heavy ceramic laboratories.** K. ZIMMERMANN. *Ber. deut. keram. Ges.*, **14** [1], 28–50 (1933).—As a result of a thorough investigation of the possibility of applying Andreasen's sedimentation apparatus in testing heavy clays, it was shown that the sedimentation analysis in the pipette apparatus is a serviceable test method which is completely preferable on several grounds to the elutriation analysis. The importance of a proper preparation of the clay is shown, especially the value of the proper peptizing medium. Tests on five different types of clay show that sodium oxalate or sodium citrate are as suitable as a sodium or ammonium hydroxide, and that with both a more complete separation of the particles and a lower dependence on the concentration of the solution can be established. Illustrated. E.J.V.

**Practical clayworking. III.** ANON. *Brit. Clayworker*, **42** [493], 37–39 (1933).—Drainage, transportation, roads, stacking grounds, hoisting, elevators, and conveyers are discussed. For Part II see *Ceram. Abs.*, **12** [7], 270 (1933). R.A.H.

**Study of apparatus for cutting brick, etc.** PIERRE RENAULT. *Rev. mat. constr. trav. pub.*, No. 283, pp. 73–75*B* (1933).—Horizontal apparatus is discussed. See also *Ceram. Abs.*, **12** [4], 166 (1933). M.V.K.

**Manufacturing brick and tile by dry pressing and by the stiff-mud process.** ANON. *Tonind.-Ztg.*, **57** [33], 380–82 (1933).—Extruding machines for roofing tile, sewer pipe, face brick, etc., should show about 12 in. inside diameter. Common brick and large-sized tile should be manufactured by larger machines. If the extruding machine is running too fast, the clay will heat and stick inside resulting in a heavy power consumption. Different types of mouthpieces are described. Faults encountered in shaping the brick are discussed. W.M.C.

**Factors that influence drier performance.** ARNOLD WEISSELBERG. *Chem. Met. Eng.*, **39**, 426–29 (1932).—The factors which enter into the performance of a drier, *i.e.*, capacity, drying rate, evaporation, diffusion, forced diffusion, and efficiency, their relations to the mechanism of drying, and the improvements which they suggest, are discussed. A Mollier water-air mixture chart is used to illustrate examples. (*C.A.*)

**Artificial driers of the "Marelli System."** ANON. *Corriere Ceram.*, **14** [2], 43–47 (1933).—The installation is made up of a series of parallel cells of varying length depending on the quality and quantity of the charge and generally heated by gas from the kiln and cooling chamber. Ventilators regulate the entrance and expulsion of gases. The trucks used are also described. M.V.K.

**Notes on installations built by Electric Resistance Furnace Co., Ltd.** ANON. *Metallurgia*, **7** [42], 202–203 (1933).—Different types of electric furnaces are described. M.V.K.

## BULLETIN

**Control of pressure in the toggle brick press.** R. E. BIRCH. Amer. Refrac. Inst. *Tech. Bull.*, No. 38, 10 pp. (1933).—B. describes the construction and principles of operation of the toggle press. The toggle and hydraulic presses are briefly compared. Data are given on the variation in brick from the same press, and a method is shown whereby the variation from mold to mold can be controlled at the feed to the charging hopper. Pressure cracking is discussed. W.E.R.

## PATENTS

**Truck for conveying brick frames.** GÜNTHER HARTMANN. U. S. 1,910,104, May 23, 1933.

**Means for detecting and marking warped tile.** J. A. BOWER (National Tile Co.). U. S. 1,910,461, May 23, 1933.

**Friction tile press.** F. B. YINGLING (Ceramic Machinery Co.). U. S. 1,910,733, May 23, 1933.

**Pottery making.** A. F. B. KOHLER (Kohler Co.). U. S. 1,911,011, May 23, 1933.

**Apparatus for drying clay, etc.** W. H. SACHS AND R. T. VORIS (Manufacturers Equipment Co.). U. S. 1,911,533, May 30, 1933.

**Sandblast nozzle.** ABRAHAM HOYLE. U. S. 1,911,571, May 30, 1933.

**Divider.** E. B. WESTON. U. S. 1,912,505, June 6, 1933. A divider consists of a plurality of crossing plates fitted into each other by coöperating slots extending respectively from their upper and lower edges and a locking device connected with the crossing edges of the plates at the top of the intersection, the device being provided with means to fit over and lock the plates in position, the locking device taking the form of a Maltese cross and being formed of a small rectangular plate, the corners of which are beveled and the slots of which extend inwardly along the diagonals from each of the corners toward and stop short of the center thereof.

**Furnace for multiple heat treatment of metals, refractories, glass, etc.** PAUL DAMIRON. Fr. 739,465, July 5, 1932. (*C.A.*)

**Laboratory muffle furnace.** V. V. BORKIN. Russ. 27,046, May 7, 1929. A laboratory furnace is provided with a preheating device for the fuel and for the air. (*C.A.*)

## Kilns, Furnaces, Fuels, and Combustion

**Monnier tunnel kiln.** ANON. *Brit. Clayworker*, **42** [493], 51–52 (1933).—One of these kilns located at the Hammill Brickworks, Kent, is internally coal fired and is at the present time firing semidry-pressed brick at about 1070°C. The kiln is 320 ft. long with an effective internal cross-section 5 ft. high x 6 ft. wide. The kiln cars are 10 ft. 4 in. long and are set with brick in 3 cross blocks or blades 3 brick (2 ft. 4 in.) thick. Between each of the blocks of green brick a space about 1 ft. wide is left into which the coal is fed from the top of the kiln. An essential feature of the firing is the grading of the coal which is such that 54% is between 10- and 30-mesh, 20% between 30- and 60-mesh, 6% between 60- and 100-mesh, and 20% passes 100-mesh. Automatic stokers, annealing of the brick, and fuel consumption are discussed. The advantage of internal firing is the great saving in fuel cost with no disadvantage to the ware. R.A.H.

**Lining of tunnel kilns.** A. MENDHEIM. *Tonind.-Ztg.*, **57** [31–32], 369 (1933).—Tunnel-kiln linings should show not only a high melting point, but also a high softening point. No additional shrinkage should occur when heating the furnace lining for a long period. W.M.C.

**Notes on automatic firing of continuous kilns.** PREVOST. *Céramique*, **35**, 229 (1932).—The conditions necessary to obtain maximum efficiency from automatic stokers are pointed out. It is essential to regulate not merely the number but also the distribution and the duration of the charges, depending upon the particular firing zone and the nature of the fuel. In the zone in front of the high fire, longer intervals are required between the charges in order to give sufficient time for the coal to burn before the next charge. The Sam-Ruetz stoker, which can be regulated so as to adapt the stoking to the progress of the fire, is briefly described. (*T.C.S.E.*)

**Performance of annular kilns.** FRIEDR. SCHÜNHOFF. *Ziegelwelt*, **64** [7], 63–65 (1933).—The work of annular kilns is discussed theoretically. M.V.K.

**Service and fuel consumption of industrial furnaces.** RICH. BRANZKE. *Feuerungstechnik*, **21** [3], 36–37 (1933).—A method for calculating fuel consumption is discussed. M.V.K.

**Modern suspended arches.** ANON. *Chem. & Ind.*, **52** [13], 279 (1933).—A description is given of the "Liptak" double suspension arch used in glass, ceramic, annealing, and other types of furnaces. See also *Ceram. Abs.*, **12** [3], 111 (1933). G.R.S.

**Firing glazed pottery in different types of furnaces.** ANON. *Tonind.-Ztg.*, **57** [34], 388–89 (1933). W.M.C.

**Gas firing of pottery.** A. MACKAY. *Pottery & Glass Rec.* [Eng.], **15** [4], 102–103 (1933); for abstract see *Ceram. Abs.*, **12** [7], 273 (1933). M.V.K.

**Firing brick by means of coal dust from locomotives.** G. ZEHNER. *Tonind.-Ztg.*, **57** [39], 453–54 (1933).—From 5 to 10% of coal dust may be added to the raw materials of brick. A careful mixture of the raw material and the dust and slow firing of the products are emphasized. W.M.C.

**Coal selection for industrial plants.** B. FRISBY. *Eng. Boiler House Rev.*, **46** [9], 586–88; [10], 644–46 (1933).—The factors governing the selection of fuel are (1) ratio of steam demand to boiler capacity, (2) capacity of ash-handling apparatus, (3)

selection of particular grades (size), (4) dry and washed fuels, (5) actual trial and the proximate analyses, and (6) calorific value and ultimate cost. The conclusions are as follows: (*a*) the ash should be as low as possible; (*b*) the fusion point of the ash must be as high as possible; (*c*) the volatile matter should be as low as will burn satisfactorily; (*d*) the calorific value should be high; and (*e*) the price, including transport and delivery charges, should give the highest possible number of heat units per unit of cost. W.E.R.

**Observations on the distribution of ash in coal and coke.** A. MARSDEN. *Gas Jour.*, **202** [3646], 54–58 (1933).—A classification of coal impurities is given tabularly. The effect of cleaning on ash content is treated. A rapid test showing ash distribution in coal is described. G.R.S.

**Production of gas and gas producers.** H. WERNICKE. *Tonind.-Ztg.*, **57** [38], 439–40 (1933).—Different types of gas producers and their use for different types of coal are described. W.M.C.

**Chemistry of gaseous fuels used for glass, enamel, and pottery. I.** JOHN W. ROMIG. *Ceram. Ind.*, **20** [5], 220–21 (1933).—R. discusses the properties of producer gas, natural gas, blue water gas, carbureted gas, and oil-still gas. Tables showing compositions and heat values of the various gases are presented. W.W.M.

**Rational method of fuel oil supply.** P. G. GRIGOR'EV. *Keram. i Steklo*, **9** [2], 16–17 (1933).—G. describes two types of fuel oil burners used in the Russian glass industry, (1) mechanical burners for tank furnaces, and (2) steam sprayers for supplementary furnaces. In both cases special equipment for the supply of fuel is required. M.V.K.

**Application of pulverized-fuel firing to cement kilns.** ANON. *Mech. World*, **92**, 405–407 (1932); abstracted in *Power & Fuel Bull.*, **22**, 139 (1932). W.E.R.

**Observations of automatic temperature control.** C. E. FOSTER. *Metallurgia*, **7** [42], 187–90 (1933).—F. considers only the system of automatic control which operates primarily by the indications of an electrical pyrometer. Details of the installation are given. M.V.K.

**Fundamentals and economies in the clay industries. XXVII.** ELLIS LOVEJOY. *Clay-Worker*, **99** [5], 172–73 (1933).—Continuing his discussion of kilns, L. takes up fire level, dimensional ratios of floor area, floor openings, stack area, stack height, primary and secondary flues, grate areas, etc., and describes the various types of mechanical stokers available for kiln firing. Results obtained in tests with stokers are discussed. For Part XXVI see *Ceram. Abs.*, **12** [7], 273 (1933). E.J.V.

**Heat convection in masonry conduits.** H. H. BÖHM. *Arch. Eisenhüttenwesen*, **6**, 423–31(1933).—Experiments were carried out on passing hot air through conduits 4 yards in length with different diameters and surface conditions. The rate of flow varied from 0.4 to 7 yards per second, temperatures ranging up to 800°C. Formulas are given for the turbulent flow, but formulas for the laminar region could not be derived. It was found that heat convection is influenced by the temperature, length, and diameter of the conduit, type and velocity of the gas, temperature difference between gas and masonry, and surface condition of the masonry. Suggestions are given for the construction of regenerators. W.M.C.

BOOK

**Heat Transmission.** W. H. MCADAMS. *Can. Chem. Met.*, **17** [2], 35 (1933); for abstract see *Ceram. Abs.*, **12** [6], 240 (1933). E.J.V.

PATENTS

**Kiln for treating earthy materials.** WARNER HATHAWAY (American Face Brick Research Corp.). U. S. 1,910,433, May 23, 1933.

**Kiln.** H. M. ROBERTSON. U. S. 1,911,089, May 23, 1933.

**Refractory lined hollow electrode.** S. T. WILES (Buffalo Electric Furnace Corp.). U. S. 1,912,560, June 6, 1933.

**Process of building brick kiln arches.** L. W. SHELHAMER (Carey Brick Co.). U. S. 1,912,662, June 6, 1933.

**Ovens or kilns for use in the manufacture of earthenware tile, brick, etc.** G. H. DOWNING AND H. R. HOLDING. Brit. 391,175, May 3, 1933.

**Firing ceramic masses.** PORZELLANFABRIK KAHLA, SWEIGNIEDERLASSUNG FREIBERG. Brit. 391,704, May 10, 1933.

**Continuous furnace for refractory products, using liquid fuel.** ÉTABLISSEMENTS BERGER CADET ET FILS. Fr. 740,238, Oct. 20, 1931. (*C.A.*)

**Tunnel muffle for making glazed pottery.** CARL DANHAUSER. Ger. 569,442, Feb. 1, 1931. (*C.A.*)

**Tunnel kiln for firing salt-glazed stoneware.** HOLDING GES. FÜR KERAMISCHE WERKE. Ger. 569,443, Dec. 13, 1927. (*C.A.*)

## Geology

**Minimum capillary rise in an ideal uniform soil.** W. O. SMITH. *Physics*, **4** [5], 184–93 (1933).—The rise of liquid into an ideal uniform soil, under the action of capillary forces, differs from the steady flow across the soil. The steady transmission of fluids takes place through the continuous capillaries extending across the soil; the rise of liquid under capillary forces is from cell to cell. The hexagonal scheme of grains spaced at a distance $(2r + d)$, where $d$ is a function of porosity, is used as a statistical representation of the soil, and the problem is discussed from the standpoint of this packing. The fluid, in its passage through the long capillaries, flows through a cyclic capillary showing definite maxima and minima in each element, and the rise from cell to cell, under capillary forces, is through a channel with definite maxima and minima. The minimum opening of a cell is the section defined by the plane of centers; the greatest is the section defined by the plane, parallel to the plane of centers, tangent to the grains of the cell immediately over the first cell. The greatest rise occurs when the minimum opening holds the meniscus and is observed by allowing the liquid to fall through the soil. The least rise should occur when the maximum opening holds the meniscus and should be observed by allowing the liquid to rise through the soil. Wetting phenomena, however, introduce complications affecting the minimum rise. Rings of liquid form just above the meniscus around the point of contact of each pair of grains and carry the rising liquid higher until it attains a position where it is no longer able to reach the rings so formed; equilibrium then prevails at a rise intermediate to the two extremes just defined. The exact conditions controlling the rise phenomena are determined. The approximation developed for the capillary equation in an earlier paper is then used with these conditions to calculate the minimum rise. The results are compared with the data given in the earlier paper, and good agreement within the experimental error is obtained.

**Chemical study of the aluminosilicates.** W. VERNADSKY. *Z. Krist.*, **84** [5–6], 337–72 (1933).—After a general discussion V. treats the chemical theory of the aluminosilicates, chlorites, and kaolin aluminosilicates and their color functions. G.R.S.

**Oxides and hydrates of aluminum.** J. D. EDWARDS AND M. TOSTERUD. *Jour. Phys. Chem.*, **37** [4], 483–88 (1933).—There is a monohydrate of aluminum, $Al_2O_3 \cdot H_2O$, other than diaspore, which is found widespread in nature and is being made commercially. Its existence can be demonstrated by chemical analysis, X-ray diffraction patterns, and thermal analysis. Other forms of alumina and its hydrates are briefly reviewed. G.R.S.

**Notes on tantalum and niobium.** W. R. SCHOELER. *Sands, Clays, & Minerals*, **1** [3], 40–42 (1933).—The properties, occurrence, mining, and obtaining of tantalum and niobium are described. The only solvent for Ta and Nb is a mixture of hydrofluoric and nitric acids. M.V.K.

**Zeolitic alteration of pyroclastics.** M. N. BRAMLETTE AND E. POSNJAK. *Amer. Mineralogist*, **18** [4], 167–71 (1933).—The frequent alteration of vitric pyroclastics to clay materials, of which montmorillonite is the most abundant, has been well established and bentonite is recognized as a rock name for such material. This paper points out that the mineral clinoptilolite, which may be included with the zeolites, is also a common alteration product of pyroclastics where the alteration is less complete. This mineral seems to be an intermediate product in the process of alteration of the volcanic glass, with the clay mineral as end product of the process. G.R.S.

**Structure of crystals.** U. DEHLINGER. *Physik*, **1** [1], 7–14 (1933).—X-rays are the most efficient means of studying the structure of crystals. For this type of work the atomic factor is of a great importance, as found by W. L. Bragg and others. This factor has been calculated from wave mechanics by Thomas, Fermi, and Hartree. In some cases electron diffraction patterns have been used for determining the structure of crystals. The structure of many complicated silicates has been found in recent years. Laws have been studied relating to the solid state, such as the binding forces between atoms, and many applications have been made. Deviations from the periodicity of the lattice of crystals have been found caused by the introduction of foreign atoms into a given lattice, cold working, and thermal treatment. Two steps distinguished in the

formation of crystals from solutions are the formation of nuclei and the growth of the crystals. Few data are available yet for recrystallization. A complete bibliography is given. W.M.C.

**Crystal structure of muscovite, $KAl_2(AlSi_3)O_{10}(OH)_2$.** W. W. JACKSON AND J. WEST. *Z. Krist.*, **85** [1–2], 160–64 (1933).—A new set of diagrams is given showing the way in which the various atoms are linked together and, while emphasizing the pseudo-hexagonal arrangement, illustrating the way in which the monoclinic character of the structure is produced. G.R.S.

**Outward form of titanite crystals.** K. BAUER. *Mineralog. petrog. Mitt.*, **43** [4–5], 319–51 (1932).—The crystal form of single and twin crystals of titanite is determined by measurement of the central distances on adjacent crystal surfaces. The differences of form of titanite occurring as rock-forming units and as cleft minerals (sphene) are easily representable. G.R.S.

**Pectography: effect of colloids on crystallization.** J. ALEXANDER. *Chem. & Ind.*, **52** [1], 3–4 (1933).—References are given to a large number of papers dealing with the subject of the effect of colloids on crystallization. G.R.S.

**General geology of the crystallines of Alabama.** G. I. ADAMS. *Jour. Geol.*, **41** [2], 159–73 (1933).—Some Triassic diabase dikes in Alabama have been mapped. A tentative interpretation of the structure of the crystallines and the relations of the more important intrusives are presented. The field work has been correlated with mapping in progress in Georgia and is offered as a basis for more detailed studies. G.R.S.

**Diatomite.** M. R. *Rev. gén. sci.*, **43** [22], 630–31 (1932).—Data on the composition, properties, deposits, and utilization of diatomite are given. M.V.K.

**Origin of the igneous rocks of Minnesota.** F. F. GROUT. *Jour. Geol.*, **41** [2], 196–218 (1933).—Analyses now available do not support the early suggestion that igneous magmas in Minnesota were formed almost in place by hydrothermal fusion of earlier rocks. Suggestions made elsewhere of such fusion of rocks in the earth's crust are briefly noted and an attempt is made to show about how far the idea of fusion in the crust can now be safely applied. G.R.S.

**Gems and gem minerals of North Carolina.** J. H. PRATT. *Amer. Mineralogist*, **18** [4], 148–59 (1933).—A list of gem minerals found in the state is followed by a discussion of (1) diamonds, (2) corundum, (3) beryl, (4) hiddenite, (5) garnet, (6) quartz, (7) opal, (8) feldspars, and (9) other gem minerals. G.R.S.

**Microscopic minerals of the clays of Middlesex County, New Jersey.** A. C. HAWKINS, A. STOLLMAN, AND L. A. BUCK. *Amer. Mineralogist*, **18** [4], 160–66 (1933).—Descriptions are given of the following minerals found in elutriated clay residues: (1) magnetite, (2) garnet, (3) hematite, (4) pyrite, (5) zircon, (6) gypsum, (7) tourmaline, (8) quartz, (9) muscovite, (10) ilmenite, (11) rutile, and (12) limonite. G.R.S.

**Micropaleontology of the Pennsylvanian Johns Valley shale of the Ouachita Mountains, Oklahoma, and its relationship to the Mississippian Caney shale.** B. H. HARLTON. *Jour. Paleontology*, **7** [1], 3–29 (1933).—This paper is published in two parts. The first part describes the calcareous algae, Foraminifera, conodonts, Bryozoa, and astracoda. The second part describes the Gastropoda, Pelecypoda, Brachiopoda, and Cephalopoda. A fossil chart is given showing the ranges of the fossils in other correlative areas. G.R.S.

**Base-replacement studies of Oklahoma shales.** L. C. CASE. *Bull. Amer. Assn. Petroleum Geol.*, **17** [1], 66–79 (1933).—Clays of an alkaline nature which contain a predominance of replaceable sodium are stated by Taylor to overlie all petroleum deposits. These shales are said to have undergone base replacement in sea water and subsequent leaching in fresh water. An examination of several Okla. shales indicates that the base replacement did not take place in ordinary sea water, that the shales were not leached, that all shales encountered in drilling in Okla. are of the one type, and that such determinations therefore have no application. G.M.H.

**The name "Lillis Formation" in California geology.** G. DALLAS HANNA. *Bull. Amer. Assn. Petroleum Geol.*, **17** [1], 81–84 (1933).—The confusion in the usage of this term applied to the shale in question is outlined. G.M.H.

**Structural features in the Columbia River lavas of central Washington.** M. G. HOFFMAN. *Jour. Geol.*, **41** [2], 184–95 (1933).—The conditions under which the lavas were extruded and the probable methods of formation of the basalts are discussed. G.R.S.

**Ancestral Rockies and Mesozoic and Late Palaeozoic stratigraphy of Rocky Mountain region.** ROSS L. HEATON. *Bull. Amer. Assn. Petroleum Geol.*, **17** [2], 109–68 (1933). G.M.H.

**Application of kieselguhr.** A. C. *Rev. gén. sci.*, No. 11 (1932); abstracted in *Rev. mat. constr. trav. pub.*, No. 277, pp. 188–89 *B* (1932).—The composition, properties, and uses of kieselguhr mined in France are discussed. M.V.K.

**Industrial Minerals Section, Canadian Institute of Mining and Metallurgy.** ANON. *Can. Mining Met. Bull.*, No. 253, pp. 286–88 (1933).—A section of the Institute has been formed to include all members interested in nonmetallics except fuels. The first meeting of this section was held on April 5 and 6 at the Annual Meeting of the Institute. G.M.H.

BOOKS AND BULLETINS

**Petrography and Petrology: a Textbook.** FRANK F. GROUT. Reviewed in *Nature*, **131** [3305], 317–18 (1933).—The book stresses the study of the life history of rocks rather than their description and classification. The petrographical portions, while subordinate to petrology, contain many good illustrations. In the petrological sections following the petrographies of the igneous sedimentary and metamorphic rocks in turn there is a fine account of modern views on the origin of rocks. See also *Ceram. Abs.*, **11** [12], 636 (1932). J.L.G.

**Metamorphism: Study of the Transformations of Rock Masses.** ALFRED HARKER. x + 360 pp. Methuen and Co., Ltd., London, 1932. 1s 6d net. Reviewed by P. Niggli in *Nature*, **131** [3305], 310–11 (1933).—The first part is devoted to thermal metamorphism. The second part deals with dynamic and regional metamorphism and contains short chapters on injection and repeated and retrograde metamorphism. J.L.G.

**Plasticity: a Mechanics of the Plastic State of Matter.** A. NADAI assisted by A. M. WAHL. Engineering Societies Monographs. Revised and enlarged from the first German edition. xxiii + 349 pp. McGraw-Hill Book Co., Inc., New York. The book is briefly reviewed in *Nature*, **131** [3307], 383 (1933); for review see *Ceram. Abs.*, **11** [2], 139 (1932). J.L.G.

**Handbook of Geophysics. Vol. III.** (Handbuch der Geophysik.) B. GETENBERG. Gebruder Borntträger, Berlin, 1930. Reviewed in *Jour. Geol.*, **41** [2], 224 (1933).—This is the third volume of a proposed ten-volume series on physical geology, the first two, the fourth, and the sixth being in press. All of the volume is well written and excellently illustrated. G.R.S.

**Textbook of Mineralogy. With an Extended Treatise on Crystallography and Physical Mineralogy.** E. S. DANA. Chapman and Hall, Ltd., London, 1932. Reviewed in *Nature*, **131** [3305], 318 (1933); for abstract see *Ceram. Abs.*, **12** [3], 126 (1933). J.L.G.

**Report on Band-Spectra of Diatomic Molecules.** W. JEVONS. The Physical Society, London, 1932. Reviewed in *Jour. Phys. Chem.*, **37** [4], 537–38 (1933). G.R.S.

**Earth History.** LUTHER C. SNIDER. "The Century Earth Science Series," edited by K. F. Mather. Century Co., New York, 1932. Reviewed in *Jour. Geol.*, **41** [3], 332–34 (1933).—The book is divided into four main sections, (1) the book of the earth, (2) history of continents, (3) history of living things, and (4) man and earth history. See also *Ceram. Abs.*, **12** [4], 171 (1933). G.R.S.

**A Chapter in Earth Science History. Geological Society of America, 1888–1930.** HERMAN LEROY FAIRCHILD. Judd and Detweiler, Inc., Washington, D. C., 1932. 232 pp. 18 plates. Price $2.50. Reviewed in *Bull. Amer. Assn. Petroleum Geol.*, **17** [1], 97 (1933). G.M.H.

**Methods of Crystal Structure Determination with the Aid of X-Rays. Vol. I. The Laue Method.** (Methoden der Kristallstrukturbestimmung mit Röntgenstrahlen.) E. SCHIEBOLD. Akademische Verlagsgesellschaft, Leipzig, 1932. Reviewed in *Z. Krist.*, **85** [1–2], 168 (1933). G.R.S.

**Outline of Mineral Paragenesis.** (Grundriss der Mineralparagenese.) F. ANGEL AND R. SCHARIZER. J. Springer, Vienna, 1932. Reviewed in *Z. Krist.*, **85** [1–2], 167–68 (1933). G.R.S.

**Treatise on Sedimentation.** WILLIAM H. TWENHOFEL, *et al.* Reviewed in *Bull. Amer. Assn. Petroleum Geol.*, **17** [1], 98 (1933); for review see *Ceram. Abs.*, **12** [6], 242 (1933). G.M.H.

**Replacement origin of the albite granite near Sparta, Oregon.** JAMES GILLULY. Geol. Surv. *Professional Paper*, No. 175*C*. 16 pp. 5¢ from Supt. of Documents, Govt. Printing Office, Washington, D. C. R.A.H.

**Barite and barium products in 1931.** R. M. SANTMYERS AND B. H. STODDARD. Bur. Mines Mineral Resources U. S. 8 pp. 5¢ from Supt. of Documents, Govt. Printing Office, Washington, D. C. R.A.H.

**Geophysical Abstracts. No. 48.** F. W. LEE. Bur. Mines *Monthly Service Rept.*, GA 48. 23 pp. 10¢. The report reviews recent publications and patents relating to geophysical prospecting methods and instruments. For No. 47 see *Ceram. Abs.*, **12** [7], 277 (1933). R.A.H.

**Contributions in Geology and Geography.** Edited by LEWIS F. THOMAS. Wash. Univ. Studies, *Sci. & Tech.*, No. 7 (1932); reviewed in *Jour. Geol.*, **41** [3], 335 (1933).—This volume includes (1) geographical landscape of metropolitan St. Louis, by L. F. Thomas, (2) geologic work of ice jams in sub-Arctic rivers, by C. K. Wentworth, (3) Opemiska granite intrusive, Quebec, by C. Tolman, and (4) synonymy of the mid-Devonian rugose corals of the Falls of the Ohio, by C. Werner. G.R.S.

**Symposium on Weathering Characteristics of Masonry Materials. Vol. 31.** The American Society for Testing Materials, Philadelphia, 1931. Reviewed in *Jour. Geol.*, **41** [3], 335 (1933). G.R.S.

**Mineral Economics.** Lectures under the Auspices of the Brookings Institution. "A. I. M. E. Series," McGraw-Hill Book Co., Inc., New York. Reviewed in *Jour. Geol.*, **41** [3], 335–36 (1933).—A series of lectures delivered under the auspices of the Brookings Institution of Washington, D. C., by fifteen well-known geologists, mining engineers, and mineral economists is recorded. G.R.S.

**International Geological and Mineralogical Calendar, 1933–1934.** (International Geologen und Mineralogen Kalender.) R. CRAMER. F. Enke, Stuttgart. Reviewed in *Jour. Geol.*, **41** [3], 336 (1933).—There are 254 pages of names and addresses in alphabetical arrangement, followed by 49 pages of data on geological surveys (arranged by continents and countries), 77 pages on universities, technical colleges, and leading museums, and 28 pages on geological societies. G.R.S.

**Clays and Shales of Oklahoma.** L. F. SHEERAR AND J. S. REDFIELD. Okla. A. & M. College Div. of Eng. *Publication*, **3** [5], 1–251 (1932).—No high-grade pottery clays but many shales with properties warranting their use for heavy clay products have been found. The physical tests and geological description of 252 more accessible clay and shale deposits are given. (*C.A.*)

**Report of the Committee on Sedimentation, 1930–1932.** Prepared under the auspices of the Division of Geology and Geography by W. H. Twenhofel, committee members, and others, Washington, D. C., 1932. 229 pp. Price $1.00. National Research Council *Bull.*, No. 89; reviewed in *Bull. Amer. Assn. Petroleum Geol.*, **17** [3], 270–72 (1933). G.M.H.

PATENT

**Production of china clay.** A. RIGBY AND A. J. HICKLING. Brit. 391,878, May 17, 1933.

## Chemistry and Physics

**Application of Blair-Leighton equation to X-rays.** J. A. LESTER AND J. M. BLAIR. *Jour. Phys. Chem.*, **37** [1], 17–20 (1933).—A different method of evaluating the ideal maximum developable density is described, and a different integral of the Blair-Leighton equation is presented. Evidence is presented that this equation also expresses the rate of formation of the latent photographic image by X-rays. G.R.S.

**Influence of combined oxygen on the adsorption of vapors by porous solids. I.** L. J. BURRAGE. *Jour. Phys. Chem.*, **37** [4], 505–10 (1933).—The coefficient for $CO_2$ was determined by the Pirani gage technique. Reasons are advanced for previous isothermals being found to consist of a series of curves. G.R.S.

**Studies on silicic acid gels. II. Time of set as a function of temperature.** C. B. HURD AND P. S. MILLER. *Jour. Phys. Chem.*, **36** [8], 2194–2204 (1932).—Time of set of various mixtures of solutions of six different commercial sodium silicates with acetic acid at four different temperatures was determined. The effect of temperature was the same regardless of the soda-silica ratio. A theory for the mechanism of formation of a silicic acid gel is suggested. **III. Effect of addition of some solutes on the time of set.** C. B. HURD AND D. H. CARVER. *Jour. Phys. Chem.*, **37** [3], 321–29 (1933).—The effects of added solutes on the time of set of gel mixtures produced by mixing solutions of acetic acid and sodium silicate were studied. An attempt was made to separate the specific effects of the compounds themselves from the effects which they produce by changing the $p_H$ of the mixtures. For Part I see *Ceram. Abs.*, **11** [5], 329 (1932). G.R.S.

**Determination of the isoelectric point.** L. V. ANDREWS AND D. J. BROWN. *Jour.*

*Phys. Chem.*, **37** [4], 417–24 (1933).—The rate of solubility and the amphoteric properties of lead oxide were studied, and a general method for measuring the isoelectric point of an amphoteric oxide was suggested. G.R.S.

**Theory of refraction shooting.** M. MUSKAT. *Physics*, **4** [1], 14–28 (1933). G.R.S.

**Diagram of the periodic table.** F. W. RIXON. *Chem. & Ind.*, **52** [12], 260–61 (1933).—The table is put forward as an aid to the study of the chemical properties of the elements in the light of their atomic structure. G.R.S.

**An improved method for the determination of isothermals by the retentivity technique.** L. J. BURRAGE. *Jour. Phys. Chem.*, **37** [1], 33–39 (1933).—An improved technique for the determination of isothermals is described. The derived isothermals were found to consist of a series of rectangular steps. G.R.S.

**Polarigraphic method shows new analytical applications.** V. MAJER. *Ind. Eng. Chem., News Ed.*, **11**, 90 (1933).—A quick method for the determination of alkalis in materials of high silica and alumina content has been worked out. The determination is made microanalytically, using tetramethylammonium hydroxide, and the time required is about forty minutes. The accuracy of the method is within +0.1% with 2% of alkalis. (*T.C.S.E.*)

**Experiments on the contact potential of zinc crystals.** W. A. ZISMAN AND H. G. YAMINS. *Physics*, **4** [1], 7–9 (1933).—Experiments were made proving for the first time that it is possible to obtain a reproducible constant potential difference on zinc in air at ordinary pressures, provided the cleaved surface of a single crystal is used. G.R.S.

**Wet and dry combustion methods for determining total carbon in soils and other materials.** NORMAN J. KING. *Chem. Eng. Mining Rev.*, **24**, 429–31 (1932).—The wet oxidation method with 30 cc. concentrated $H_2SO_4$, 20 cc. $H_3PO_4$, and 100 g. $CrO_3$ in 100 cc. of water is preferred and the necessary manipulation is described in detail. It is recommended to absorb the $CO_2$ in 25 cc. of *N* NaOH, and at the end titrate the excess after adding $BaCl_2$ to precipitate $BaCO_3$. (*C.A.*)

**Determination of the total surface area of soils, clays, etc.** H. KURON. *Kolloid-Beihefte*, **36**, 178–255 (1932); for Parts I and III see *Ceram. Abs.*, **11** [2], 136 (1932). **IV. Combination of water in the several horizons of different soil profiles.** *Z. Pflanzenernähr. Düngung u. Bodenk.*, **24A**, 257–77 (1932). **V. Hysteresis in water adsorption.** *Ibid.*, **25A**, 179–87 (1932).—Relationships between the process of water adsorption and the nature of the soil profile and depth of the horizons are examined. Profiles of different types show definitely different values, but there is little change with varying depth in the same profile. The hysteresis phenomena recorded are dependent on the sensitiveness of the soil colloids to drying out, the action of enclosed air in reducing adsorption rates, and the swelling of the colloids. (*C.A.*)

**Determination of crystal orientation.** J. THEWLIS. *Z. Krist.*, **85** [1–2], 74–88 (1933).—A description is given of a graphical method of calculating the crystallographic indices of a crystal. Formulas are also given for making the calculation without graphs. G.R.S.

**Crystal structure of aluminum halides. I. Crystal structure of $AlF_3$.** J. A. A. KETELAAR. *Z. Krist.*, **85** [1–2], 119–32 (1933).—$AlF_3$ crystallizes in the rhombohedral system. The structure of the unit cell is based on X-ray diagrams. A model of the structure is shown. G.R.S.

**Determination of silicon, aluminum, fluorine, and orthophosphoric acid in the presence of one another. II.** T. MILLNER AND F. KUNOS. *Z. anal. Chem.*, **92**, 253–64 (1933).—De Boer and Basart have proposed a method for determining F in the presence of Si and Al which depends upon the fact that $F^-$ discharges the color of the lake formed with Zr and hydroxyanthraquinones. For determining small quantities of F, *e.g.*, 1 mg., it is necessary to work in solutions much less acid than those used by De Boer and Basart. Directions are given for applying the method to the determination of F in complexes such as $Na_2SiF_6$ and $Na_3AlF_6$. In the presence of $H_3PO_4$, the F can also be determined by the Zr-alizarin method if the $H_3PO_4$ is removed under optimum conditions as $Ag_3PO_4$ and the excess Ag removed with NaCl. For the determination of $H_3PO_4$ the method of Woy is applicable after the Si has been volatilized as $SiF_4$. For Part I see *Ceram. Abs.*, **12** [6], 243 (1933). (*C.A.*)

**Volumetric determination of aluminum.** J. CLARENS AND J. LACROIX. *Bull. soc. chim. France*, **51–52** [5], 668–70 (1932); abstracted in *Chim. & ind.*, **29** [4], 789–90 (1933).—The method consists in precipitating the alumina of an aluminum salt by an alkali. Two cases are described: (1) aluminum is dissolved in a surplus of the acid,

and (2) the solution is treated with helianthin. This method may be used also if the solution contains some metals such as calcium and magnesium. M.V.K.

**Colorimetric determination of phosphoric acid in alumina products.** P. URECH. *Z. anal. Chem.*, **92**, 81 (1933).—The colorimetric determination of phosphorus depends on the fact that the molybdenum-phosphoric acid complex formed on mixing a dilute phosphate solution (slightly acidified with $H_2SO_4$) with a $MoO_3$ solution is reduced to a lower oxide on adding a reducing agent. This compound is blue in color. The method is described in its application to hydrated and calcined alumina, bauxite, etc. It has the advantage of being quicker and simpler than the gravimetric method. (*T.C.S.E.*)

**Determination of boron in silicate rocks and minerals.** I. P. ALIMARIN AND I. I. ROMM. *Trans. Inst. Econ. Mineral.* (U.S.S.R.), No. 53, pp. 5–44 (in German pp. 45–46) (1932).—A critical review of the various methods used for the determination of B shows that Chapin's method of distilling the B as $Me_3BO_3$ into NaOH solution and then titrating the excess NaOH with HCl is by far the best. Some modifications, such as the addition of a few drops of HCl in the presence of an indicator to the $Me_3BO_3$ before distillation to neutralize the CaO resulting from the addition of $CaCl_2$, are recommended. A description is given of a new method in which distillation with MeOH is replaced by extraction of the NaOH fusion with hot water and removal of cations other than B with $(NH_4)_2CO_3$. Fusion and extraction must be repeated twice for complete extraction. Titration is completed as in Chapin's method. (*C.A.*)

**Determination of potassium by the cobalt nitrite method.** W. U. BEHRENS. *Z. Pflanzenernähr. Düngung u. Bodenk.*, **24A**, 289–93 (1932).—The volumetric determination of $K_2O$ by oxidizing the $K_3NaCo(NO_2)_6$ precipitate in acid solution with an excess of $KMnO_4$, and subsequently titrating with oxalic acid, is recommended as accurate. (*C.A.*)

**Color test for cobalt.** A. CHIAROTTINO. *Industria chimica*, **8**, 32–33 (1933).—A Co solution treated with a dilute alcohol solution of benzidine or with an alcohol solution of dimethylglyoxime does not become colored, but if these two are added together a beautiful orange-red coloration results. This test will identify 0.01 mg. Co and must be carried out in neutral solution. Ni can be removed at the start by adding excess dimethylglyoxime. Cu and Cr interfere, giving precipitates. The reagent is prepared by dissolving 0.5 g. benzidine and 0.25 g. dimethylglyoxime in 100 cc. of 95% EtOH. (*C.A.*)

**Structural relationships of silicon compounds on the basis of tetrahedral domains of atoms.** RICHARD REINICKE. *Z. Krist.*, **82**, 394–418 (1932).—On the assumption that the Si domain is tetrahedral (like that of C in diamond), structures are deduced for cubic and hexagonal SiC, $\alpha$-cristobalite, tridymite, and quartz glasses. In considering the structures of silicates in general, R. differs from Bragg in that he considers that the Si atoms play the chief rôle, rather than a close packing of O atoms. Tetrahedral domains are also proposed for N, F, O, and Ne. See following abstract. (*C.A.*)

**Tetrahedral field of force of atoms.** R. REINICKE. *Ann. Guébhard-Séverine*, **6**, 141–50 (1930).—A theory of molecular structure on the basis of regular tetrahedral atoms is advanced. (*C.A.*)

**Piezoelectric determination of the breaking strength of fine metal, glass, and quartz fibers.** F. SEIDL. *Z. Physik*, **75**, 735–40 (1932).—A quartz plate lies between two electrodes; the upper one has the shape of a bow. To it is fixed the fiber whose breaking strength is to be measured; the other end of the fiber carries an Fe sphere. Below the latter is placed a small electromagnet. The tension of the fiber can be varied by the current flowing through the electromagnet and is measured by the charge of the quartz crystal by using a quadrant electrometer. If the magnetic field is increased, the light spot of the electrometer wanders on the scale and turns suddenly when the fiber tears. The breaking strength can be read from the scale as it can be calibrated by application of known pressures on the quartz crystal. (*C.A.*)

**The equilibrium $2MnO + Si \rightleftharpoons SiO_2 + 2Mn$.** W. KRINGS AND E. KEHREN. *Z. anorg. allgem. Chem.*, **209** [4], 385–408 (1932).—The ideal mass law does not suffice for the representation of the equilibrium between metal and slag in the three-component system Mn–O–Si. In the region from 0 to 60% $SiO_2$ in the slag, the equilibrium may be expressed by the constant $K = \frac{(MnO)^2\,(Si)}{(SiO_2)(Mn)^2} = 0.113$. At a higher $SiO_2$ content the constant decreases. The equilibrium was studied in crucibles of $Al_2O_3$, $ZrO_2$, and MgO. $Al_2O_3$ crucibles have hardly any effect on the equilibrium; $ZrO_2$ and MgO crucibles tend to lower the value of the constant due to solution of those oxides.

L.T.B.

**The course of the reaction in the solid state.** I. WEYER. *Z. anorg. allgem. Chem.*,

**209** [4], 409–28 (1932).—The course of mineral formation was followed in a dry mixture of the composition $CaO \cdot SiO_2$. Reaction between $CaCO_3$ and $SiO_2$ begins at 600 to 650°. CaO is formed first, and then $2CaO \cdot SiO_2$ forms; it is present in the $\beta$- and not the $\gamma$-form. At 735° $\beta$-$2CaO \cdot SiO_2$ is the reaction product and only after long tempering does monosilicate occur. At 815 to 835° monosilicate forms directly. At higher temperatures (1050 to 1250°) monosilicate forms exclusively. The heats of formation of the compounds were determined. The course of the reaction was followed by means of X-rays supplemented with microscopic determinations. L.T.B.

**The quantitative determination of CaO, $3CaO \cdot SiO_2$, $2CaO \cdot SiO_2$, $3CaO \cdot 2SiO_2$, $CaO \cdot SiO_2$, and $SiO_2$ in the presence of each other.** WILHELM JANDER AND ERNA HOFFMANN. *Angew. Chem.*, **46** [4], 76–80 (1933).—A chemical method for the quantitative determination of these compounds in the presence of each other is given. Titration in various solutions is employed for the determination. The limit of error for the silicates is about 3% while that of CaO and $SiO_2$ is less. L.T.B.

**X-ray studies on the behavior of BaO-SrO mixtures on heating.** W. G. BURGERS. *Z. Physik*, **80** [5–6], 352–60 (1933).—On heating $BaCO_3$ and $SrCO_3$, solid solutions of the oxides may be formed by diffusion. The solid solution series is incomplete. The lattice constant behaves as a linear function of the composition. The volatilization of BaO from the surface layer of a mixture of the oxides and the effect of solid solution formation on the chemical-crystallographic configuration were studied. L.T.B.

**Vapor pressure measurements of BaO, SrO, CaO, and their mixtures from measurements of the rate of volatilization.** A. CLAASSEN AND C. F. VEENEMANS. *Z. Physik*, **80** [5–6], 342–51 (1933).—The authors give expressions from which the vapor pressures of these may be determined over a limited range of temperature. Measurements on mixtures of BaO with SrO and BaO with CaO show that these oxides are completely miscible. L.T.B.

**Rate of decomposition of zinc oxalate into ZnO, $CO_2$, and CO.** GUSTAV F. HÜTTIG AND EDELBERT LEHMANN. *Z. phys. Chem., B*, **19** [6], 420–26 (1932).—The rate of decomposition of zinc oxalate was studied at 405, 360, and 325° with and without the removal of the gases formed. The rate of decomposition in vacuum may be expressed by the relation $\frac{dn}{dt} = kn^{2/3}$. The effect of additions of chromium oxide to the zinc oxalate, the effect of a partial pressure of $CH_3OH$, and the effect of the removal of the gas phase are discussed. L.T.B.

**Changes of magnetic and X-ray spectroscopic properties during the change of a mixture of zinc oxide and iron oxide into spinel.** HERBERT KITTEL AND GUSTAV F. HÜTTIG. *Z. anorg. allgem. Chem.*, **210** [1], 26–32 (1933).—The changes in the magnetic and spectroscopic properties when $ZnFe_2O_4$ is formed from a mixture of the oxides are studied. The course of the reaction was studied by means of X-rays. L.T.B.

**Practical calculations for mixing and diluting.** HEINRICH MENZEL. *Chem. Fabrik*, pp. 289–90 (1932).—A geometrical method of obtaining desired percentages is explained by diagrams and calculations. (*C.A.*)

**Closest packings of higher order.** E. K. BROCH. *Z. Physik*, **78**, 257–70 (1932).—A system of equal spheres may be arranged not only in the well-known cubic or hexagonal forms but in an infinite number of arrangements which are less symmetrical but have the same mean density. These closest packings of higher order seem to be realized in some minerals. (*C.A.*)

**A decade of applied X-ray research.** G. L. CLARK. *Chem. & Ind.*, **52** [15], 317–25; [16], 336–46 (1933).—An address is presented. G.R.S.

## BOOKS

**Measurement of Air Flow.** E. OWER. 2d ed. 243 pp. 85 illustrations. Chapman and Hall, Ltd., London. Price 15s. *Colliery Guard.*, **146** [3777], 919 (1933).—The book deals extensively with the design and use of the Pitot tube, vane anemometers, and manometers, and should therefore be of great value to the mine ventilation engineer. Other chapters of the book deal with such matters as the flow of air in pipes, measurements of flow and resistance, plate orifice, Venturi tube, nozzle, and other questions of air-flow measurement. O. has developed his mathematical formulas in a straightforward fashion. E.J.V.

**The Method of Dimensions.** A. W. PORTER. Methuen and Co., London, 1933. Reviewed in *Jour. Phys. Chem.*, **37** [4], 538 (1933).—A historical introduction stressing the fundamental work of Newton, and later, Fourier, leads the way to discussion of such problems as the flow of liquids, surface tension, and heat effects. A final section deals with electromagnetic and electrostatic units. G.R.S.

**Physical Chemistry.** JOHN EGGERT. Translated by S. J. Gregg from the third edition of "Lehrbuch der physikalischen Chemie" revised in collaboration with Lothar Hock. xi + 632 pp. Constable and Co., Ltd., London, 1932. 24s net. Briefly reviewed in *Nature*, **131** [3308], 419 (1933). J.L.G.

**Physico-Chemical Handbook.** (Physikalisch-chemische Taschenbuch.) Published by C. Drueker and E. Proskauer. Vol. 1, viii + 546 pp. 29 M. Vol. 2, viii + 481 pp. 17 M. Akademische Verlagsgesellschaft m.b.H., Leipzig, 1932–1933. Reviewed in *Nature*, **131** [3315], 676 (1933).—The Physico-Chemical Handbook is divided into nine sections as follows: structure of matter, optics, electricity, magnetism, microchemics (molecular physics), macrochemics, chemical statics, dynamics, heat, and systematics of inorganic and organic chemistry. It consists of a series of reviews of present knowledge in these sciences and the methods of measurement now in use with equations for applying them. J.L.G.

**Dictionary of Colloidal Chemistry.** (Worterbuch der Kolloidchemie.) ALFRED KUHN. Theodor Steinkopff, Dresden, 1932. Reviewed in *Jour. Phys. Chem.*, **37** [1], 150–51 (1933).—The method of treatment lies between a dictionary and an encyclopedia, the more important topics being treated in greater detail. G.R.S.

**Gmelin's Handbook of Inorganic Chemistry. Vol. 8. System-Number 30: Barium.** (Gmelin's Handbuch der anorganischen Chemie.) Deutschen Chemischen Gesellschaft, Berlin, 1932. Reviewed in *Jour. Phys. Chem.*, **37** [4], 538–39 (1933); see also *Ceram. Abs.*, **11** [10], 544 (1932). G.R.S.

**The Sorption of Gases and Vapors by Solids.** J. W. MCBAIN. Geo. Routledge and Sons, London, 1932. Reviewed in *Jour. Phys. Chem.*, **37** [1], 149–50 (1933); see also *Ceram. Abs.*, **11** [12], 640 (1932). G.R.S.

**Chemical Analysis of Iron and Steel.** G. E. F. LUNDELL, J. I. HOFFMAN, AND H. S. BRIGHT. John Wiley and Sons, New York, Chapman and Hall, London, 1931. Reviewed in *Trans. Faraday Soc.*, **29** [4], 591–92 (1933); for abstract see *Ceram. Abs.*, **11** [7], 431 (1932). G.R.S.

**Applied X-Rays.** G. L. CLARK. 2d ed. McGraw-Hill Book Co., New York, 1932. Reviewed in *Jour. Phys. Chem.*, **37** [4], 541–42 (1933). G.R.S.

### PATENTS

**Manufacture of silicon-diamino tetrafluoride.** S. S. SVENDSEN (Clay Reduction Co.). U. S. 1,911,004, May 23, 1933. (1) The method of removing silica from materials containing it consists in subjecting the material in the dry way to the action of ammonium fluoride in quantity less than that required for complete conversion of the silica into fluosilicate, thereby converting the silica into silicon-diamino tetrafluoride ($SiF_4 \cdot 2NH_3$) and volatilizing the silicon-diamino tetrafluoride. (2) The step in the removal of a metal in the group including silicon, vanadium, and titanium from materials containing oxygen compounds thereof comprises heating such material with ammonium fluoride under dry conditions at a temperature high enough to form fluoride ammonia compounds of metals of the group and volatilizing the fluoride ammonia compounds. (3) The step in the treatment of a siliceous oxygen compound comprises heating at least sufficient ammonium fluoride in the dry way with the compound to volatilize substantially all the silicon therefrom.

**Production of monocalcium phosphate and dicalcium phosphate.** E. I. DU PONT DE NEMOURS & CO. Brit. 391,495, May 10, 1933.

**Aluminates.** ERIK L. RINMAN. Fr. 740,621, July 30, 1932. Solutions of $NaAlO_2$ practically free from $SiO_2$ are prepared by digesting bauxite, etc., with a solution of NaOH in the presence of oxides or hydroxides of Ba, Sr, Ca, Mg, Zn, or their mixtures, preferably in excess of that required to precipitate the $SiO_2$, and with the addition of $Na_2CO_3$. (*C.A.*)

**Fluosilicates.** BRANDER FARBWERKE, CHEMISCHE FABRIK G.M.B.H. Fr. 741,502, Aug. 24, 1932. Fluosilicates, such as $ZnSiF_6$, are made by the action of $H_2SiF_6$ on the metal, such as Zn, in the presence of a catalyst composed, *e.g.*, of reduced Cu. (*C.A.*)

## General

**Tribute to Boothe Colwell Davis.** EDITORIAL. *Bull. Amer. Ceram. Soc.*, **12** [6], 161–63 (1933).

**Sell American-made ware.** EDITORIAL. *Bull. Amer. Ceram. Soc.*, **12** [6], 163–65 (1933).

**Ceramics exposition at Rutgers University.** ANON. *Bull. Amer. Ceram. Soc.*, **12** [6], 208–12 (1933).—Illustrated.

**Testing methods for ceramic materials.** LOTHAR KRÜGER. *Ber. deut. keram. Ges.*, **14** [1], 1–16 (1933).—K. describes several methods of testing different properties of ceramic materials and compares them as to results obtained. It is pointed out that the values for the individual properties of materials obtained by different test methods vary to a considerable extent. Their true evaluation is possible only when it is stated by which method they were obtained. The test methods are so constructed that the test values give a key to the practical testing and that the key can also be authentically shown, *i.e.*, the results obtained in the laboratory are directly comparable with one another. This is attainable, however, only by exact standardization of the processes, necessary standardization of apparatus, and similar evaluation of test results to numerical values, as well as by setting up standards of quality from similar viewpoints. Illustrated. E.J.V.

**Ceramics in home construction featured at A Century of Progress.** ANON. *Ceram. Ind.*, **20** [5], 232 (1933).—Porcelain enameled steel, glass brick, and structural plate glass are being used as building materials in exhibition homes at A Century of Progress. Ceramics are also being used in the interiors. A list of all the homes to be exhibited is included. W.W.M.

**Cooling time in absorption tests. I.** ANDRÉ LAVERGNE. *Rev. mat. constr. trav. pub.*, No. 283, pp. 61–65*B* (1933).—L. discusses in detail different methods used in the U. S., Germany, and Czechoslovakia in absorption tests of liquids by ceramic products. M.V.K.

**Acid-resisting chimney construction.** MAURICE BARRETT. *Brit. Clayworker*, **42** [493], 40–42 (1933).—The corrosive gases primarily responsible are sulfurous acid gas and sulfuric acid mist. They react with the lime or Portland cement first near the top of the chimney and form gypsum resulting in a considerable increase in volume. Most acid-resisting cements do not resist atmospheric attack for long. A satisfactory contruction is an inner cavity lining extending the entire length of the chimney with efficient ventilation in the cavity to prevent accumulation of adventitious stagnant gases. This construction is described and illustrated and a construction specification is given. R.A.H.

**Cardox.** S. G. NAISH. *Can. Mining Met. Bull.*, No. 254, pp. 365–87 (1933).—The Cardox method is a new and revolutionary process of dislodging coal at the working face using carbon dioxide gas as the blasting medium. The method is fully described. G.M.H.

**Choice of heat-insulation materials.** A summary of a paper by A. LINDSAY FOSTER. *Brit. Clayworker*, **42** [492], 25–26 (1933).—The temperature gradient in furnace walls of several insulating materials and the expansion of insulating materials under heat and their efficiency are discussed. R.A.H.

**Plastic steam insulation.** J. S. GANDER. *Mech. World*, **92** [2375], 29–30 (1932).—The chief insulating materials which are used in high-temperature steam practice are asbestos, magnesia, and kieselguhr. M.V.K.

**Problems facing the manufacturer of roofing tile.** A. HOFHERR. *Tonind.-Ztg.*, **57** [31–32], 365–66; [34], 391–92 (1933).—Economic problems resulting from the decrease in output of many brick plants are discussed. Better advertising methods are suggested. Psychological factors are outlined for promoting an understanding between the manufacturer and the user of roofing tile. The protection of buildings by roofing tile is illustrated in the case of near-by fires. Illustrated. W.M.C.

**Adequate lighting makes better workers.** A. L. LYMAN. *Ceram. Ind.*, **20** [5], 236–40 (1933).—Inspection of finished products, delicate color shading operations, and decorating work all demand the right kind of light for good workmanship. The value of adequate illumination is discussed and various lighting installations are described. W.W.M.

**How to maintain floors for greatest net profit. I.** H. L. SCHULTZ. *Maintenance Eng.*, **91** [2], 33–36 (1933).—Illustrated by charts, photos, and tables. J.L.G.

**Coördination of research, sales, and production.** R. F. WILDER. *Management*, **54**, 4*b* (1932); abstracted in *Mech. Eng.*, **54** [11], 800 (1932).—W. shows how various research activities are coördinated with one another and as a unit with sales and production. F.G.H.

**Computing clay plant costs.** GEORGE A. MAYS. *Brick Clay Rec.*, **82** [5], 161–62 (1933).—A method of cost accounting which takes into account the various factory costs as they occur under some or all of seven manufacturing functions is outlined and discussed in detail. E.J.V.

**Distribution of labor in manufacturing refractories.** H. KREMSKI. *Tonind.-Ztg.*, **57** [36], 415–16 (1933). W.M.C.

**Lubrication bills too high.** JOHN W. SHAVER. *Factory Management & Maintenance*, **91** [3], 82–84 (1933).—S. describes how the B. F. Goodrich Rubber Co. since 1920 has decreased its lubrication expense 67% per 1000 lb. of raw rubber processed. A development department for testing and compounding greases and oils and a lubrication foreman who assigns definite areas to individual oilers are features of the system. Illustrated. J.L.G.

BOOK AND BULLETIN

**Supply of Water.** T. H. P. VEAL. Chapman and Hall, London, 1931. Reviewed in *Chem. & Ind.*, **52** [1], 16 (1933).—This book deals with the principal sources of water, the classification of impurities, and the methods and plants used for softening, filtering, and sterilizing water both for domestic and industrial use. G.R.S.

**Silicosis and tuberculosis among miners of the tri-state district of Oklahoma, Kansas, and Missouri for the year ended June, 1929.** F. V. MERIWETHER, R. R. SAYERS, AND A. J. LANZA. Bur. Mines *Tech. Paper*, No. 552, 28 pp. 5¢ from Supt. of Documents, Govt. Printing Office, Washington, D. C. The report deals with the relation of certain infectious diseases to silicosis, production rate of silicosis, and progress in controlling silicosis and tuberculosis. R.A.H.

*35th Annual Meeting*

**THE**

# AMERICAN CERAMIC SOCIETY

**Week of February 11**

## Hotel Netherland Plaza

**Cincinnati, Ohio**

***Eight Divisions Meeting Simultaneously***

**All on One Floor**

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The Division Program Committees are busy and the assurances are that this will be a high record meeting.

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